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SLUDGE BLANKET ADSORPTION PROCESS FOR THE REMOVAL OF REFRACTORY CONTAMINANTS FROM WASTE WATERS

Ionac Chemical Company, Birmingham, N. J.

December 1962

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IONAC CHEMICAL COMPANY
a division of PFAUDLER PERMUTIT INC.
Birmingham, New Jersey

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J. N. WILLIAMSON - A. H. HEIT - C. CALMON

FINAL TECHNICAL REPORT
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The feasibility of using cheap, commercially available substances for treatment of waste waters, especially sewage effluents, was investigated. Minerals, industrial by-products, proteinaceous substances, conventional water treatment agents, etc. were tested. Activated carbon was used as a reference. Some minerals exhibited minor affinities for the organic solute phase of secondary sewage effluents. Minerals treated with salts of tetravalent metals showed promise for this purpose. Tables and a 239-item bibliography are included.

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SLUDGE BLANKET ADSORPTION PROCESS FOR THE REMOVAL OF REFRACTORY CONTAMINANTS FROM WASTE WATERS

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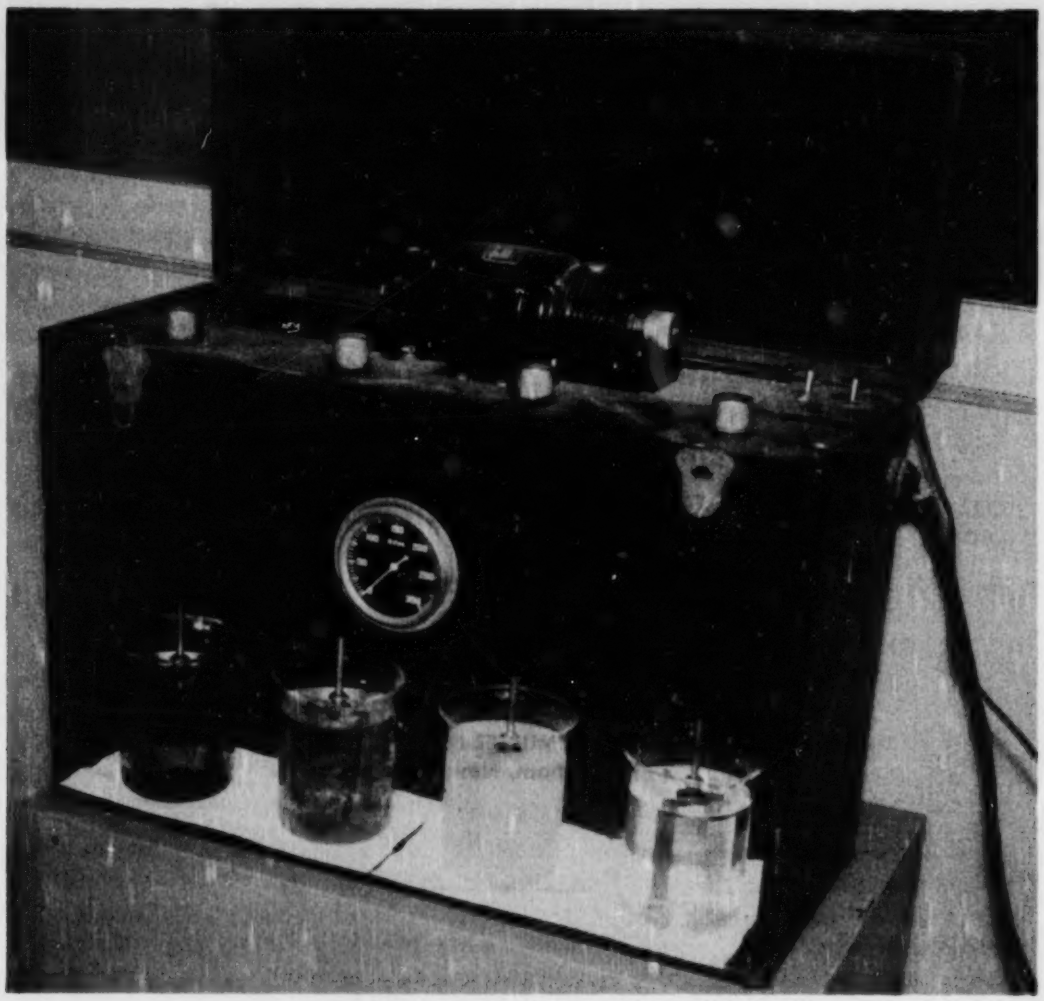

Figure 1. - Jar-type batch testing apparatus.

Beakers (left to right):

(a) activated carbon treatment

(b) protein-ferric compound coagulation

(c) lime treatment

(d) treated water.

ABSTRACT

An investigation was undertaken to learn whether cheap, commercially available substances hold promise in the treatment of waste waters, especially secondary sewage effluents. Minerals, industrial by-products, proteinaceous substances, conventional water treatment agents, etc. were tested. Activated carbon was used as a reference in this study.

Some minerals exhibited minor affinities for the organic solute phase of secondary sewage effluents. Minerals treated with salts of tetravalent metals showed promise for this purpose.

Most conventional coagulants exhibit marked affinities for the refractory organic substances present in secondary sewage effluents. Proteins evidence similar properties when coagulated in the presence of mineral acids and certain acid salts of trivalent metals. Hydrophobic proteins, aldehyde-hardened in granular shape then further reacted with acids or acid salts will also remove organic refractory substances from secondary sewage effluents. These substances can be used in bed form and are regeneratable.

Organic anion exchangers will also remove organic solutes from sewage. The problem of irreversible organic fouling requires more attention here if they are to be considered in such advanced waste treatments. Pre-coagulation of the higher molecular species of organics is suggested as a fouling preventative measure.

This study also demonstrated the feasibility, at least from a mechanical standpoint, of incorporating solid adsorbents into the sludge blanket process for water treatment in the presence or absence of coagulants. The sludge blanket process can combine the virtues of the finely-divided, high surface area forms of solids and flocs (normally associated with batch treatment techniques or vacuum filtrations) with the maintenance of high flow rates, normally associated with columnar bed techniques.

Material cost factors are discussed for the various substances tested and the treatments involving their use. Recommendations are made for possible further lines of investigation.

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1. INTRODUCTION

1.1 Background

Present day sewage treatments result in secondary effluents, which are discharged into receiving streams, rivers, or bays, and sludges which are burned or spread on the soil. The secondary effluents invariably contain small amounts of substances which have resisted efforts to degrade or otherwise render them innocuous. Accordingly, these materials, termed "refractory substances", build up in concentration in waters as the waters are used and reused.

As the population increases, the water supply can only remain relatively constant. Coastal areas, and areas with nearby bodies of brackish water are beginning to turn to the purifying of high salinity water to increase their water supplies. In general, however, all areas are right now faced with the necessity of more and more water reuse and the problems resulting therefrom. Increases in (a) production of domestic, industrial, and agricultural wastes; (b) synthesis and use of difficultly degradable (or undegradable) organic compounds; and (c) water consumption are compounding these problems with a resultant buildup of refractory substances in water supplies.

To combat the problems of refractory contaminants, biologically degradable materials can in some cases be substituted into common usage for difficultly degradable materials. In many cases, however, this would be a backward step. The most probable ultimate solution of the refractory substance removal problem, would appear to lie in the direction of more advanced water and sewage treatment measures.

Many studies in the removal of refractory substances from waters have been or are being undertaken. This list includes use of such techniques as ion exchange and adsorption, coagulation, oxidation, electrodialysis, electrolysis, foam fractionation, and distillation. The ultimate goal of all work being undertaken via these techniques is a process (or combination of processes) whereby direct reuse of water with no natural body of water serving as an intermediate carrier-can be made commonplace.

1.2 Object of this Investigation

This investigation was undertaken to learn

(a) Whether any cheap, commercially available substances or materials (such as, but not limited to, industrial by-products or scrap, or naturally occurring minerals, clays, earths, and the like) possess the capability of adsorbing, or otherwise removing, the refractory substances present in waters which have been reused-especially domestic secondary sewage effluents and

(b) Whether these substances, if proven useful for this purpose, might best be utilized in a sludge-blanket process.

The sludge blanket process is considered a likely technique for taking advantage of any adsorptive or ion-exchange properties of cheap solid substances, since these properties no doubt would be best exhibited in the finely divided state. A columnar bed, for example, would have to consist of larger particles with a smaller surface area to bed volume ratio in order to get an adequate flow rate.

This study was not limited to solid materials, of course. Substances were tested, whether in liquid, solid, or gaseous form, or in solution. The main criterion stressed was massive refractory substance removal at low cost. Accordingly, coagulation and oxidation formed integral parts of these experiments.

1.3 Approach Employed in this Investigation

1.3.1 Primary Emphasis Throughout Study

The primary emphasis throughout this study was placed on removal of organic refractory substances, as evidenced by the dichromate reduction method for determination of chemical oxygen demand (C.O.D.). Chloride and other inorganic ions were recognized as potentially refractory substances. Accordingly, tests were conducted to determine if any inorganic substances were being removed in the course of each treatment tested. Frequently, substitution of inorganic for organic substances was given consideration where it was known that the inorganic substances thus imparted into the water could be removed at a very low additional-treatment cost. In addition to the C.O.D. test, testing procedures employed included analyses for chloride ion, dissolved solids, total solids, alkyl benzene sulfonate detergents (A.B.S.) and pH.

Testing procedures were in accordance with "Standard Methods for the Examination of Water and Wastewater" Eleventh Edition, 1960.

1.3.2 Literature Survey

The first step in this project was to survey the literature. Pertinent references to treatment and reuse of waters, especially sewage, were noted and recorded. Of special interest, of course, were references to substances which would be amenable to the sludge blanket process. Emphasis was therefore placed on such topics as adsorption, ion exchange, coagulation, and oxidation, with less attention being given to references concerning such topics as electrodialysis, electrolysis and foam fractionation.

1.3.3 Effluent Waters Used in this Study

1.3.3.1 Sewage Effluents

The sewage effluent used in these experiments was secondary sewage effluent, largely of domestic origin, but with a few small industries contributing to it. This effluent was obtained from the Mt. Holly, N.J. Sewage Plant. Due to the limited size of the receiving stream, (the Rancocas Creek) the treatment facilities in this plant include chlorination to control pathogens. Cross-checks of testing procedures were occasionally run with effluent obtained from the 32nd and Farragut Streets Sewage Plant in Camden, N.J. No chlorination step is included in the production of this Camden sewage effluent, which is discharged into the Delaware River. For the most part the effluent was filtered (via a vacuum filtration employing Whatman #5 paper) prior to experimental treatment.

Flow diagrams of the sewage treatment plants are depicted in Figures 6 & 7.

1.3.3.2 Synthetic Laundramat Effluent

For purposes of investigating the effect of some substances on A.B.S., some tests were conducted with a synthetic laundramat effluent. This was done to approximate the conditions under which A.B.S. is associated with other compounds and substances in some trade effluents. This synthetic laundramat effluent contained the following:

60 ppm of standard A.B.S. (100% basis), 200 ppm Na_3PO_4 4 ppm of NaOCl, 5 ppm of sodium carboxy methyl cellulose, 5 ppm urea, 5 ppm $(NH_4)_2CO_3$, 100 ppm of $CaCl_2$, 30 ppm of $MgSO_4$, and 50 ppm of NaCl.

1.3.3.3 Rancocas Creek Water

In one instance, the highly colored water of the Rancocas Creek at Birmingham, N.J. was employed to test a substance. This liquor was prefiltered through Whatman #5 paper. The purpose here was to note the affinity of the substance for the color bodies (largely humates and humic acids) present in the water. It is believed by the authors that high molecular weight acids and their salts, similar to (and possibly in some cases identical to) humic acids and humates, also account for a major portion of the organic refractory substances present in secondary sewage effluents(142, 236, 237).

1.3.4 Effluent Treatments

Effluent treatments, which varied according to the nature of the material being tested, were set up to screen the long list of materials selected for testing. Testing procedures included batch or jar tests, columnar beds, and sludge blanket treatments. The screening tests were so designed as to place the effluent samples in contact with a given material in a manner which could be duplicated (for testing and comparing effects of materials of a similar nature). Time factors were held constant to simulate practical detention times in an actual process treatment. The ratio of the weight of the treatment material under study to the weight of the effluent being treated was varied, especially if an initial test of the material indicated the pertinancy of determining Freundlich isotherm data for purposes of economic evaluation of indicated treatment dosages.

Where screening data indicated a material to be potentially useful in lowering the refractory substance content of the effluent, combination treatments (often involving the use of conventional water treatment chemicals), were tried. Such multi-component treatments were designed to establish

(a) Whether or not this promising material is removing the same contaminants as the complementary treatment materials and

(b) Whether or not synergistic effects can be produced in a system wherein the promising material is employed.

Most such multi-component treatments involved simultaneous treatment of the effluent by the materials in a one-stage treatment. Some tests were conducted in a series of stages, however, wherein the effluent was treated first with one material, then with another material, and so on.

Synthesis and testing of novel compounds and materials were undertaken during this study. Such novel products were prepared from cheap, commercially available raw materials, in an effort to

(a) Enhance previously established properties of refractory substance removal possessed by the raw materials and

(b) To adapt a material (or materials) in a way which will overcome inherent disadvantages to its use in the sludge blanket process or other continuous-flow systems. (See Figure 5).

2. TECHNICAL DISCUSSION

2.1 Nature of Substances to be Removed

Secondary sewage effluents generally contain only about 0.05% of substances other than water(236). Various efforts to analyze these substances have resulted only in pin-pointing a few according to their exact composition. Many must therefore be listed according to similar structural groups or other characteristics which they possess. Some of these substances have been found to be A.B.S., proteins, carbohydrates, tannins, lignins, long chain hydrocarbons and long chain fatty acids. Essentially they are anionic or non-ionic organic substances. Some inorganic substances, notably chlorides, are also represented here, however.

2.2 Mechanisms of Removal which are Amenable to the Sludge Blanket Process

2.2.1 Adsorption and Ion Exchange

Many of these substances can be adsorbed onto clays and other minerals. The adsorption process need not impart other substances to the effluent. Cationic resins (anion exchangers) will also lower the concentration of these substances in secondary sewage effluent. Three main problem areas are encountered here, however. They are (1) organic fouling (2) disposal of regeneration wastes and (3) removal of exchanged ions from the effluent. Anionic resins (cation exchangers) can be of some value in eliminating these substances from sewage plant discharge waters, especially in the H^+ form. The prime mechanism involved here is believed by the writers to be an "in situ" coagulation effect, wherein the coagulated substances are adsorbed or otherwise held onto the surface of the resin. If this is the case, this class of exchangers could hold much promise, since they would have fewer of the inherent disadvantages of the anion exchangers. It might be necessary, however, to present a cation exchanger to an effluent in a much more finely divided state than that of an anion exchanger.

2.2.2 Coagulation

Coagulants and coagulant aids, ideally, would form the basis of a sludge blanket process for removal of refractory substances from sewage effluents. Continuous coagulation, wherein a sludge blanket is built up and held constant, is the very heart of the sludge blanket process for water treatment. The coagulated solids present an enormous surface area for adsorption to take place. Finely divided solids-also liquids or solutions, can simultaneously be fed into the sludge blanket apparatus to supplement the work of the coagulants and coagulant aids in the removal of refractory substances. These supplementary additives, can be oxidants, as well as adsorbents or ion exchangers.

While continuous coagulation may be desirable, it is not essential. A material can be prepared, which would have the nature or character of a sludge blanket, and utilized in the sludge blanket apparatus. The more complex the mixture contained in the sludge blanket apparatus the more difficult becomes the task of separating the components for regeneration and reuse, where applicable.

2.2.3 Oxidation

Oxidation can feasibly be utilized in the sludge blanket process simultaneously with coagulation, adsorption, and ion exchange. Agents for increasing oxygen transfer can be utilized to assist in the work of the oxidizing agents.

2.3 Substances and Formulations tested via Batch, Columnar Bed, and Sludge Blanket Treatments

2.3.1 Adsorbents in Batch Testing

Most of the adsorbents tested were samples obtained from commercial suppliers and manufacturers. The mean particle size was approximately 325 mesh, mostly ranging from 200 to 400 mesh. The following adsorbents were tested as received (without altering or modifying them in any way other than grinding and screening where necessary):

(a) Aluminates

Calcium Aluminate

(b) Carbonates

Limestone

(c) Carbons and Coals

Ionac C-150 - sulfonated coal type cation exchanger.

Nuchar C-190-N - activated carbon, vegetable origin.

Animal Charcoal (Bone black)

(d) Ion Exchange Resins

Ionac A-540 (Cl^- form)

Ionac A-300 ($SO_4^=$ form)

Permutit ZP (K^+ form)

(e) Industrial Wastes, By-Products

Flyash, boiler and chimney,
Ionac Chemical Co., Birmingham, N.J. Plant

Flyash
Cincinnati Gas and Electric

Cement (stack) dust
Southwestern Portland Cement Co.

(f) Metal Oxides

- Ilmenite
- Rutile-milled and ceramic
- Bauxite-calcined and uncalcined
- Zirconium oxide

(g) Phosphates

- Calcium phosphate
- Monazite

(h) Silicas

- Diatomaceous earths
- Perlites
- Silica flour

(i) Silicates

- Kaolinite
- Aluminum-silicate pigments
- Vermiculite
- Mica
- Panther Creek bentonite
- Wyoming bentonite
- Greensand
- Manganese zeolite
- Desertalc
- Attapulgites
- Molecular sieve powder
- Decalso
- Yellow gel

(j) Sulfates-"Rare earth sodium sulfate" (a sulfuric acid extractive of monazite ore containing cerium).

The following adsorbents, as modified or prepared in the laboratory, were tested:

(a) Metal oxides

Zirconia, hydrous ZrO_2

(b) Silicas

Amine-treated diatomaceous earth

(c) Silicates

$ZnCl_2$-treated vermiculite

H_3PO_4-treated Panther Creek bentonite

$ZnCl_2$-treated Wyoming bentonite

$Zr(SO_4)_2$-H_2SO_4-treated Wyoming bentonite

$Zr(SO_4)$-H_2SO_4-treated uncalcined Pikes Peak clay

$ZnCl_2$-treated greensand

$ZnCl_2$-treated bauxite, uncalcined

$ZnCl_2$-treated attacote

2.3.2 Coagulants and Coagulant Aids in Batch Testing

The following coagulants and coagulant aids were tested in accordance with the well-known techniques of water clarification by coagulation:

Reten

Separan 2610-A

Rosin Amine D Acetate

Isodecyl Diethylene Triamine Acetate

Alum

Ferric Sulfate

Ferric Chloride

Proteins

Titanium Tetrachloride

Calcium Oxide

2.3.3 Oxidants and Oxygen Transfer Agents in Batch Testing

The following oxidants were tested:

Air-with and without methyl isobutyl carbinol-as an oxygen transfer agent, added to the sewage effluent.

Ferrate-prepared in lab.

Potassium Permanganate

Sulfuric Acid

2.3.4 Combination Batch Treatments

The following agents were tried in combination treatments:

Panther Creek Bentonite plus titanium tetrachloride

Ferric Chloride followed by activated carbon (Nuchar C-115)

Potassium Permanganate plus ferric chloride followed by activated carbon (Nuchar C-115)

Potassium Permanganate followed by activated carbon (Nuchar C-115)

Rutile (milled), in sulfuric acid; plus barium carbonate plus sodium carbonate plus ferric chloride

2.3.5 Columnar Bed Testing

The following substances were tested in columnar beds:

- Ion Exchangers
    - Ionac A-300-medium base granular anion exchanger
    - Ionac A-540-strong base bead type anion exchanger
    - Ionac XLA-400-experimental strong base bead type anion exchanger
    - Ionac A-260-weak base granular anion exchanger
    - Ionac C-240 (H^+ form)-standard sulfonated polystyrene bead type cation exchanger
- Modified Proteinaceous Substances
    - Various combinations of proteins (casein, soybean protein, glutens, glues, or gelatins) with ferric compounds (ferric chloride or ferric sulfate), mineral acids, alum, and lime were tested. Aldehyde crosslinking of these substances, for purposes of stability, was emphasized.
- Minerals
    - Diatomaceous earth
    - Synthetic zeolite, diatomite, and perlite treated with amine acetate
- Activated Carbon
    - Ionac P-50

2.3.6 Sludge Blanket Testing

Only the more promising materials, as evidenced by results obtained in screening tests of the batch and columnar bed types, were tested in the sludge blanket apparatus. The materials so tested were:

Modified proteinaceous substances, hardened and unhardened

Titanium Tetrachloride

Protein plus Ferric Sulfate (fed separately)

Protein plus Ferric Chloride (fed separately)

Protein plus Titanium Tetrachloride (fed separately)

3. METHODS AND RESULTS

3.1 General

As previously mentioned, the screening tests were so designed as to place the effluent samples in contact with a given material in a manner which could be duplicated with physically similar materials.

While some work was done with synthetic laundramat effluent and Rancocas Creek water, for the purpose of further evaluating specific parameters, secondary sewage effluent remained the principle liquor employed in these tests. Initially, it was felt by the writers that the filtration of the secondary sewage effluent through a fine paper, such as Whatman #5, would be undesirable for purposes of this study. The reasons for this belief were as follows:

(a) The particulate matter would be removed in sludge blanket filtration anyway.

(b) The particulate matter might enhance coagulation and adsorption effects in the sludge blanket treatment process.

(c) Filtration through Whatman #5 paper would produce effluents which would vary in their content of the more finely divided particles. The passage of these fine particles through the paper would be regimented by the thin film or "cake" of larger particles as it builds up on the surface of the filter paper. This cake would vary in porosity and thickness depending on (1) the amount of sewage passed through the paper and (2) the quantitative distribution range of the particles in an effluent according to size and concentration; which will vary from one effluent sample to another.

We can cite the following results of C.O.D. tests on filtrate increments of secondary sewage effluent as evidence that filtration of the effluent introduces a variable-and that this variable makes it difficult to evaluate C.O.D. lowering effects of treatments where the drop in C.O.D. is not too great:

Table 1

C.O.D. of a Filtered Secondary Sewage Effluent as a Function of the Volume Continuously Passed Through Whatman #5 Paper

560 ml. through Whatman #5 paper: C.O.D. = 155 mg/l.

700 ml. through Whatman #5 paper: C.O.D. = 144 mg/l.

1300 ml. through Whatman #5 paper: C.O.D. = 122 mg/l.

Prior to filtration, the above effluent exhibited a C.O.D. of 246 mg/l.

We began our testing procedures using unfiltered secondary sewage effluent. This practice was virtually abandoned, however, for the use of pre-filtered (Whatman #5 paper) secondary sewage effluent. This was done for the obvious purposes of preventing the reduction in C.O.D. due to filtration from being confused with reduction in C.O.D. due to treatment, and preventing fouling of the surfaces of the adsorbents by those sewage particles to which these surfaces need not be exposed. It was done also for the more subtle purposes of contributing more data to those investigators whose work involves systems where prefiltering is necessary, and to standardize a phase of our testing procedure to the end that our data would more easily be compared with that of other investigators.

An insufficient amount of data was accumulated, while using unfiltered liquor, to conclude whether or not the particulate matter can enhance removal of refractory substances via the mechanism of adsorption, if appropriate additives were used. It is conceivable that these unfiltered solids would be beneficial in providing "seeding" effects to coagulation procedures, thereby lessening the dosage requirements of some coagulants and coagulant aids. It is also conceivable that at least some oxidants, if applied to the effluent in the presence of these particles, would be required in larger dosages due to oxidation effects on the particles as well as the substances in solution.

3.2 Batch Testing

3.2.1 Adsorbents

3.2.1.1 Adsorbent Testing with Synthetic Laundramat Effluent

Initial testing was begun to determine the expected action of various substances when employed in the sludge blanket filtration process for the removal of refractory contaminants from waste waters, especially secondary sewage effluents. The object of these tests was to establish:

1. a desirable range of particle size, in the case of solid adsorbents, to prevent carryover during start-up.
2. to compare the effects on sewage effluent of various substances which can be used in the sludge blanket filtration process.
3. to establish detention time for continuous treatment of a given increment of effluent within the equipment.

Two Spaulding type laboratory bench model precipitators were set-up (Figure 2) as described and depicted in a paper by Carpenter and Porter(11). The precipitators were tested to ascertain the most desirable adsorbent particle size for use therein. It was determined that particles of from 5 to 50 microns in diameter should be used in the testing of insoluble solid materials in these precipitators in the absence of a coagulant. Particles of this size appear to be large enough, so that they do not wash out of the apparatus in the effluent. They are also small enough to assure that their properties of adsorption and ion exchange, will be satisfactorily utilized.

Initial tests were run to learn what improvement might be expected in naturally occurring substances if they were activated with mineral acids. The tests were simple, consisting of rocking the effluent-adsorbent mixture from side to side in a half-full 1-liter jar (tilting down to a 45° angle, and then up to a 45° angle 50 times) then allowing to settle for 20 minutes. In lieu of sewage effluent, which had not been obtained at that stage, a synthetic "laundramat" effluent was used containing 60 ppm of alkylbenzene sulfonate and the proportionate amount of phosphates as is found in commercial detergents. Five-hundred ml. aliquots of this effluent (containing 0.03 g. A.B.S.) were treated with 0.03 gm. of adsorbent, and with 0.12 gm. of adsorbent. The results obtained were as follows:

Table 2

Effect of Some Adsorbents on a Synthetic Laundramat Effluent Containing 60 ppm A.B.S.

ADSORBENT	RESIDUAL ABS
Panther Creek Bentonite, 0.03 gm.	47 ppm
Panther Creek Bentonite, 0.12 gm.	47 ppm
Panther Creek Bentonite (H_3PO_4 activated) 0.03 gm.	32 ppm
Panther Creek Bentonite (H_3PO_4 activated) 0.12 gm.	32 ppm
Activated Carbon, Pulverized (coal product) 0.03 gm.	60 ppm(?)
Activated Carbon, Pulverized (coal product) 0.12 gm.	25 ppm

3.2.1.2 Adsorbent Testing with Unfiltered Secondary Sewage Effluent

A 5 gallon sample of the finished effluent from the Mt. Holly, New Jersey Sewage Plant was obtained and analyzed for chemical oxygen demand (C.O.D.), total solids, and solids non-volatile after 2 hours at 500°C. This effluent had a C.O.D. of 206 mg/liter, a total solids content of 400 ppm and a non-volatile solids content (after 2 hours at 500°C.) of 270 ppm. After one week at room temperature the analyses had remained essentially unchanged.

Preliminary tests were run employing several powdered adsorbents to compare their effect on the Mt. Holly Sewage effluent. The tests were run as with the above described synthetic mixture. Five-hundred ml. of the sewage effluent were treated with 0.208 g. of each adsorbent. This weight was selected, rather arbitrarily, because it represents the weight of the total solids content of 500 ml. of the sewage effluent. Settling times were varied.

It was determined that the 20 minute settling period following the rocking agitation is insufficient. Tests on the upper part of the settled effluents indicate that the "point of least returns" from settling occurs at about 30 minutes. For example, untreated effluent, with a C.O.D. of 206 mg/liter after settling for 20 minutes, has a C.O.D. of 186 mg/liter. After 30 minutes, the C.O.D. is reduced to 157 mg/liter, but after 90 minutes the C.O.D. had been further lowered to only 151 mg/liter. After 90 minutes settling, followed by filtration through a fast-flow grade of filter paper (E and D 615), the C.O.D. of the untreated effluent was further reduced to 141 mg/liter. By contrast, a treatment with 0.208 g. of Panther Creek Bentonite (American Colloid Co.), including a settling period of only 20 minutes and no filtration, lowered the C.O.D. to 122 mg/liter. The results of similar tests with this, and other naturally occurring substances, are shown in Table 14.

All are to some extent effective, as tested, in reducing the C.O.D. of the sewage effluent beyond that which can be expected by mere settling. No significant decrease in the total solids content of the sewage effluent was noted in this preliminary testing of adsorbents.

3.2.1.3 Adsorbent Testing with Secondary Sewage Effluent Pre-Filtered Through Whatman #5 Paper

The preliminary testing procedure with unfiltered secondary sewage effluent left much to be desired as a standard procedure for purposes of comparative testing of adsorbents. While pre-filtration of the effluent through a fine paper (Whatman #5) may produce somewhat variable liquors, it nevertheless can be expected to remove particles which would settle in less than 90 minutes. Pre-filtering of the effluent, therefore, serves to eliminate some doubt concerning whether the substances removed from sewage during the adsorbent tests were in solution or were present as finely divided solids.

Pre-filtering of the effluent through Whatman #5 paper was begun and adhered to throughout the balance of this study, almost without exception. In addition, all batch adsorbent testing which followed the aforementioned preliminary tests were conducted as follows:

> 500 ml. of filtered (Whatman #5 paper) secondary sewage effluent were placed in a 600 ml. beaker. A weighed amount of the adsorbent to be tested was placed in the sewage. The mixture was agitated at 50 R.P.M. for 50 minutes with a paddle agitator device (see Figure 1). After this contact period, the treated effluent was filtered through E and D 615 paper. The filtrate was then tested for refractory substances as indicated by the test for C.O.D. (along with any

supplementary tests deemed pertinent). This result was compared with the values on the untreated filtered effluent.

Before adopting these procedures, tests were run to establish the comparative effects of a post-settling period versus a post-filtration through E and D 615 filter paper. Activated carbon (Nuchar C-190-N) powder was selected for these tests. The procedures employed and the results of these tests are as follows:

Table 3

Comparison of Post-Filtration vs. Post-Settling Period, on Treated Sewage Effluent

Effluent Used in Test	Treatment	C.O.D. After Treatment Mg/L.
Secondary Sewage Effluent. Not Pre-Filtered- Initial C.O.D. = 246 mg/L.	(1) Contacted for 50 minutes at 50 RPM with 400 ppm of NU-CHAR C-190-N ACTIVATED CARBON. Post-filtered through E & D 615 paper. No settling period.	109
	(2) Contacted for 50 minutes at 50 RPM with 400 ppm of NU-CHAR C-190-N ACTIVATED CARBON. Settled for 16 hours. No post-filtration.	115
Secondary Sewage Effluent. Pre-filtered through Whatman #5 paper- Initial C.O.D. (after prefiltration) = 140 mg/L.	(3) Same as Treatment #1, above.	80
	(4) Same as Treatment #2, above.	81

This method for comparing adsorbents was also employed to determine whether pre-chlorination of secondary sewage effluent can be expected to have an effect on an adsorbent treatment. Nuchar C-190-N powder was again selected for use in comparative studies of chlorinated versus unchlorinated sewage.

A one-half gallon sample of Mt. Holly sewage effluent was taken immediately prior to chlorination and another immediately following chlorination. The time lag between taking each of these samples approximated the time interval during which the effluent passes from the point at which it was sampled prior to chlorination to the point at which it was sampled after chlorination. Tests on these samples were completed within four hours after sampling. These tests revealed no significant differences, between the chlorinated and unchlorinated effluents, which would appreciably affect the C.O.D. test, or the adsorption of contaminants by activated carbon. In Table 15 are outlined the tests which were run on these effluent samples and the results of those tests.

The adsorbents tested via these batch treatment procedures (without prior modification of the adsorbents) and the results of each test are outlined in Table 16.

Attempts were made to enhance the adsorptivity of some cheap materials by modifying them or imparting other substance onto them. The results obtained in batch-testing of these materials are also tabulated in Table 16.

Some of the natural substances were treated with a 20% aqueous zinc chloride solution for 10 minutes, washed, and dried, then used to treat filtered sewage effluent. Results obtained were not promising, but this, together with known anion-exchanging properties of certain zirconium compounds, led to testing of some zirconium-treated substances. Hydrous Zirconia which is known to possess these properties, was freshly prepared in the laboratory by mixing $Zr(SO_4)_2$ and NaOH solutions, then washing the precipitate. The moist precipitate was used to treat filtered sewage via the batch-testing procedure.

Powdered Wyoming bentonite and uncalcined Pikes Peak clay were agitated for 10 minutes in a 20% aqueous solution of $Zr(SO_4)_2 \cdot 4H_2O$ containing about 1% H_2SO_4 on the total solution weight. The clays were then filtered, washed thoroughly with distilled water, and dried. The dry, treated clays were then ground in a mortar and used to treat filtered sewage effluent. A comparison of the C.O.D. values of the sewage effluent before and after treatment indicates that zirconium-treated clays, notably Wyoming bentonite, remove considerably more C.O.D.-imparting substances than when not treated. The zirconium-treated Wyoming bentonite also appears to compare favorably with hydrous zirconia in lowering the C.O.D. of filtered sewage. However, the performance of Nuchar C-190-N was not matched by zirconia or zirconium-treated clays.

A sparsely soluble alkylated polyamine was imparted onto diatomaceous earth and tested to establish whether or not it would remove sewage contaminants. It was hoped that this amine would adhere to the diatomaceous earth, without the necessity of crosslinking, and pick-up C.O.D. imparting substances. Such apparently was not the case, however. Instead of lowering the C.O.D. of the effluent, a batch treatment of sewage with this material considerably increased the C.O.D. of the sewage. The amine employed here was isodecyl diethylene triamine. The thought was that the amine and adsorbed substances could be burned off and the base carrier reused.

Attempts were made to convert a wood shaving and sawdust mixture into a cheap adsorbent by treatment with:

1. Sodium Bisulfite
2. Sodium Hypochlorite followed by ammonia.

The $NaHSO_3$ treatment was done to try to effect a mild sulfonation of the wood, while the $NaOCl-NH_3$ treatment was tried in the hope of incorporating weakly cationic groups into the wood structure.

In general, the procedure followed was to make up an aqueous solution of the compound, place the wood into it, add sufficient water to just cover the wood, mix thoroughly, and allow several hours contact time. After the contact period, the treated wood was washed with demineralized water. In testing the adsorptivity of the washed treated wood, a weighed, damp portion was added to the sewage and, after treatment, was removed, washed, dried and reweighed to establish the dosage used, on the dry basis.

Sodium Bisulfite Treated Wood

A mixture of wood shavings and sawdust was soaked at room temperature in a 4.5% solution of sodium bisulfite as $NaHSO_3$. After 40 hours, a portion of the mixture was washed with demineralized water. 10,800 ppm (dry basis) of the washed treated wood was used to treat filtered sewage effluent with a C.O.D. of 85 mg/l. This treatment raised the C.O.D. of the sewage to 191 mg/l. After an additional 120 hours in contact with the $NaHSO_3$, another portion of the treated wood was washed. The test was repeated, this time using 2600 ppm (dry basis) of the wood on sewage effluent with a C.O.D. of 72. This treatment raised the C.O.D. of the sewage effluent by 42 mg/l. to a value of 114 mg/l. However a "blank" was also run, using 2300 ppm of the treated wood (dry basis) on demineralized water with no C.O.D. The purpose of the blank was to measure the extent to which the wood yielded oxidizable materials to the solution. The treated wood imparted 33 mg/l. of the C.O.D. to the demineralized water. Theoretically, the C.O.D. of demineralized water, treated as in the case of the sewage with 2600 ppm of the wood (instead of 2300 ppm), would be 35 mg/l. Assuming then, that 35 mg/l. of C.O.D. would also have been imparted into the sewage, and not 42 mg/l., the possibility of an exchange of wood components for sewage components becomes apparent. However, in attempts to verify this, no chloride or sulfate could be exchanged for wood components.

Sodium Hypochlorite and Ammonia Treated Wood

The NaOCl-NH_3 treatment of the wood mixture was done as follows:

> 10.0 gm. of NaOCl in aqueous solution was mixed with demineralized water in an amount estimated to be sufficient to wet 90.0 gm. of the wood. 90.0 gm. of the wood was then placed into this mixture, and sufficient additional water added to just cover the mixture. After thorough mixing, a 20 hour contact time was allowed, then the mixture was washed with demineralized water. After washing, 15.0 g. of NH_3 was added to the wood. The NH_3 was added in a 29% aqueous solution. After four hours contact time, the mixture was divided into two portions. One portion was left in contact with the NH_3 for 72 more hours, while the other portion was immediately washed free of excess NH_3. 4000 ppm (dry basis)

of the wood having four hours in contact with the NH_3 was used to treat 500 ml. of filtered sewage effluent with a C.O.D. of 72, and 500 ml. of demineralized water with no C.O.D. value. After this treatment, the C.O.D. of the sewage effluent was 81, and the C.O.D. of the demineralized water was 12. This indicates a possible C.O.D. reduction of 3 mg/l., assuming the C.O.D. imparted by the treatment is not due to refractory substances and could easily be removed by aeration, etc. It was ascertained, also, that no chloride or sulfate could be exchanged for any SO_2 or NH_3 which might have been incorporated into the components of the wood. Longer contact times with the ammonia gave no better results.

This procedure was also tried with 5.0 gm. of NaOCl to 95 gm. of wood with no more success.

3.2.2 Batch Testing of Coagulants and Coagulant Aids

3.2.2.1 General Procedure

The testing procedure for coagulants was much the same as the procedure employed with the solid adsorbents. A 500 ml. aliquot of the filtered sewage was placed in a 600 ml. beaker and agitation at 100 RPM was begun. The coagulant was then added and the speed of agitation reduced to 50 RPM. The overall contact time with agitation was 50 minutes, during which time pH adjustments with acids and/or bases were made when deemed necessary.

Following the contact period, the treated effluent aliquots were filtered through E & D 615 paper.

The batch testing procedures, employed with adsorbents and coagulants, as well as with oxidants (which are considered later) were intended to be as similar as possible for purposes of comparing results. The results of the batch coagulant tests are summarized in Tables 17 and 18.

3.2.2.2 Organic Substances

Many organic coagulants and coagulant aids are commercially available. Synthetic products, especially the polyelectrolytes, are employed in water treatment in very modest dosages. They can therefore be regarded as being relatively cheap by virtue of the fact that, where applicable, they do not contribute substantially to the overall treatment cost. This is true even though the price, per pound of these substances, is much higher than the price per pound of most inorganic coagulants, such as lime, ferric chloride, and alum. For example, dosage requirements of only 5 to 10 ppm are common for these organic substances, while dosages of 30 to 100 ppm are required in the case of many inorganic coagulants. Costly pH adjustments are often avoidable where these substances are used, also.

Evaluation of the effect of these substances in treatment of secondary sewage effluent is difficult. This is because of their solubility. Any excess of an organic coagulant or coagulant aid, which remains in solution following a treatment, contributes to the final C.O.D. of the treated effluent. Accurate testing procedures for each residual synthetic organic coagulant and coagulant aid in treated sewage are not currently available. Some measure of their effectiveness can be gained, however, by limiting the testing of these substances to dosages in the 5 to 10 ppm range, and ignoring the contribution to overall C.C.D. of their residue in solution.

This procedure cannot be followed in the case of proteins, however. Even the more hydrophobic proteins are difficult or impossible to precipitate in concentrations of less than 25 ppm.

A test for residual protein, based on reduction of the protein and consequent production of gaseous N_2, is feasible. However, no emphasis was placed on this test during this study for the following reasons:

1. time limitations
2. both the economic removal of the residual protein, and the economic pre-modification of the protein (to prevent soluble fractions from being imparted into the treated effluent), were reasoned to be more immediately pertinent for the purposes of this study.

Proteins and protein products were extensively tested via the batch coagulation procedure. In the course of testing, variations in pH, and contact time before and after pH adjustment, were tried. The purpose of these variations was to learn how residual protein, or residual organic substances from protein products, can be minimized in the treated effluents. Coprecipitation of the protein with a ferric compound was stressed.

The following protein mixtures were used in these experiments:

Mixture #1; approximate composition

5 parts NaOH
42 parts corn gluten
10 parts water
48 parts starches, oils, etc.

Mixture #2; approximate composition

6 parts CaO
42 parts corn gluten (The gluten source was GLF 40% gluten feed supplement)
10 parts water
48 parts starches, oils, etc.

Mixture #3; composition

20.0 gms. of casein dissolved in 2% NaOH solution and diluted to 100 ml. with 2% NaOH solution.

Mixture #4; (Dispersed Zein)

10.0 gms. zein (corn gluten protein) and 0.3 gm. of NaOH in 100 ml. of aqueous solution (heated to 70°C. to effect dispersion)

Mixture #5; (Dispersed Casein)

10.0 gms. of casein, 1.0 gm. NaOH, diluted to 100 ml. with water.

Mixture #6; (Dispersed Soya Protein)

10.0 gms. of soya protein diluted to 100 ml. with 1% NaOH solution.

Mixture #7; (Dispersed Gluten)

5 gm. of 70% food grade gluten (100% basis) in a 200 ml. aqueous NaOH solution. The gluten was pre-leached with 22 ml. of 0.12N NaOH solution.

Casein could not be precipitated from demineralized water at the 50 ppm level in the presence of 30 ppm $Fe_2(SO_4)_3$ when the pH was adjusted to 3.1 with H_2SO_4. Soya protein could not be precipitated from demineralized water at the 50 ppm level in the presence of 30 ppm $FeCl_3$ when the pH was adjusted to 3.3 with 1:1 HCl.

Coagulant testing controls were run employing tap water, with no C.O.D., in the belief that the electrolyte content therein might aid coagulation.

The results of these protein coagulation studies are summarized in Table 18.

Rosin Amine D acetate was tested for its affinity for A.B.S. in a synthetic laundramat effluent containing 60 ppm A.B.S. It was found that 33 ppm of Rosin Amine D acetate will lower the A.B.S. content of this effluent to 10.9 ppm and 66 ppm Rosin Amine D acetate will lower the A.B.S. content to 1.7 ppm. The precipitate is essentially colloidal and could not be removed by an alum coagulation. A diatomite filtration reasonably clarified the treated effluent, however, employing 1% of diatomite on the weight of the effluent.

Batch coagulation tests of the affinity of Rosin Amine D acetate for refractories in pre-filtered (Whatman #5) sewage effluent were tried. Dosage levels were at 25, 50, and 100 ppm of Rosin Amine D acetate. Following each treatment the effluent was filtered, employing 1% diatomite on the weight of the effluent. A control was also run on the pre-filtered sewage by measuring its C.O.D. following a similar diatomite filtration. The results of these tests are as follows:

Table 4

Batch Treatment of Pre-Filtered Secondary Sewage Effluent with Rosin Amine D Acetate

Dosage of Rosin Amine D Acetate, p.p.m.	C.O.D. of Effluent After Treatment, Mg./L.
None (Control)	93
25	130
50	135
100	(analysis not completed. Dichromate reduced more (much darker) in treated effluent than in control).

Similarly treated effluents were passed through beds of ion exchangers in an effort to remove any residual amine. These treatments are considered later.

Batch treatments of (penta) isodecyl diethylene triamine acetate on both the 60 ppm A.B.S. synthetic laundramat effluent and pre-filtered sewage were tried. No precipitate resulted in either case, and no removal of A.B.S. or other refractory substances was effected.

3.2.2.3 Inorganic Substances

The C.O.D. lowering effects of lime (CaO), in varying dosages, on pre-filtered (Whatman #5 paper) secondary sewage effluents are summarized in Figure 8. It is significant to note that this curve bears more similarity to solid adsorbent curves, for example Nuchar C-190-N (Figure 9), than to other coagulant curves. The maximum effective dosages for both lime and Nuchar

C-190-N, as indicated by these tests appears at about the 500 ppm level. By contrast, however, ferric chlorides, ferric sulfates, and alum are most effective at dosages of about 100 ppm. These coagulation tests with lime were carried out with no pH adjustments. That is, no effort was made to control the pH change effected by the lime itself.

Coagulation with ferric chloride and ferric sulfate is most effectively carried out at a pH level of about 3.0, and with alum at about 6.0. Accordingly, most coagulation tests during this study, which employed these coagulants, involved pH adjustments with hydrochloric or sulfuric acids to obtain the desired pH. The results of the testing of $FeCl_3$, $Fe_2(SO_4)_3$, and $Al_2(SO_4)_3$ are to be found in Table 17.

Unlike ferric compounds and alum, titanium tetrachloride readily forms a floc in water with no adjustment in pH.

3.2.3 Oxidants and Oxygen Transfer Agents

Evaluation of the effects of oxidants and oxygen transfer agents on secondary sewage effluent, as with organic coagulants and coagulant aids, is difficult. It was previously mentioned that the addition of an organic treatment agent to a secondary sewage effluent can result in a residue of that compound being left in the effluent after treatment. In the case of organic substances, a falsely high C.O.D. can result. The same is true of some organic oxidants, while the reverse is true of some inorganic oxidants.

Ferrate VI having hexavalent iron, was prepared from elemental Fe and $NaNO_3$(227, 237). 592 ppm was employed in the treatment of unfiltered secondary sewage effluent by the technique employed in the preliminary batch tests. That is, the sample was "rocked" 50 times then left to settle for 90 minutes-after which it was filtered through E & D 615 paper. After this treatment, the C.O.D. of the effluent was 133 mg/l. A control aliquot of the same effluent when settled for 90 minutes had a C.O.D. of only 116 mg/l.

Potassium permanganate was tried as an oxidant. 30, 60, 90, and 120 ppm of $KMnO_4$ were added to each of four 500 ml. aliquots of unfiltered sewage effluent. The aliquots were agitated with the paddle agitators for 50 minutes. The minimum dosage aliquot contained 30 ppm. The permanganate was not readily reduced. After 40 minutes, the characteristic pink tint was destroyed by the addition of a very minute crystal of cupric sulfate and of manganous chloride. The C.O.D. of the effluent following this treatment was 194 mg/l. A control aliquot of the same effluent, when settled for 90 minutes exhibited a C.O.D. of 117 mg/l.

Hydrogen peroxide was tried as an oxidant on Mt. Holly secondary sewage which was pre-filtered through Whatman #5 paper. Following the filtration, the C.O.D. of the effluent was 115 mg/l. Ten ppm of H_2O_2 were added to a 500 ml. portion of the filtered effluent and the mixture agitated for 10 minutes at 50 RPM with a paddle agitator. Following this treatment the C.O.D. had risen to 121 mg/l. The main purpose of testing the effect of a peroxide on sewage effluent, was to learn if any reactions would occur which would render the refractory substances more easily removed by ion exchange. Batch tests employing a combination of a peroxide treatment with powdered ion exchange resin (Ionac A-540) were run, and are considered later in this report.

The use of dispersed air in the presence of an oxygen transfer agent was also tested. This test was conducted with two 900 ml. samples of unfiltered sewage, into which air was passed by means of sintered glass air dispersion tubes for a two hour period. Agitation was maintained at 160 RPM for this period. One of the samples was employed as a control, while the other had 6.6 ppm of methyl isobutyl carbinol added prior to the period of bubbling and agitation. Following the two hour treatment period, both the control and the sewage containing methyl isobutyl carbinol were filtered through Whatman #5 paper. The C.O.D. of each was then measured. The control aliquot exhibited a C.O.D. of 80 mg/l. while the portion containing the carbinol had a C.O.D. of 82 mg/l. The results of this test cannot be considered conclusive, however, since much foam was produced in both portions of sewage. This foam was removed because of its stability. It is possible that the methyl isobutyl carbinol dose was removed early during the bubbling-agitation period along with the foam.

In the above tests of oxidants and oxygen transfer agents, higher C.O.D. values were recorded after treatment than before. Some explanation of this becomes apparent when the substances tested and the testing procedure are pondered more closely. Residual H_2O_2 will reduce the hexavalent chromium in the C.O.D. test. In the case of Ferrate VI and $KMnO_4$ treatments, the rise is no doubt due to the partial oxidation of particulate matter, which would have been removed by a Whatman #5 paper pre-filtration. This partial oxidation of particulate matter could serve to impart more soluble, incompletely oxidized organic matter into the effluent than the overall oxidation treatment fully oxidized. While the testing procedures employed in evaluating oxidants leave much to be desired, it is believed that these approaches offer a more valid basis for comparing one oxidant with another at comparable dosage levels, than a procedure employing a pre-filtration of the effluent. This belief is based on the need for specific tests to analyze and correct for the presence of residual treatment agents present in treated effluents.

3.2.4 Combinations of Substances

None of the batch treatments in this study were successful in removing all of the substances which impart C.O.D. to secondary sewage effluent. A few treatments, involving combinations of substances were tried early in this study(employing secondary sewage effluent which was not pre-filtered.) The purpose of these tests was simply to learn if a batch treatment, using additives, might be expected to result in the treated effluent having little or no C.O.D. A batch test with a given dosage of an adsorbent will give an investigator only one point on a Freundlich Isotherm curve. Most of the substances on which batch tests were run during this study were tried at only one dosage level. Having run one batch test on these substances, further testing was done only when the substance showed sufficient promise as a potential agent for economical removal of refractory substances from secondary sewage effluent. Nevertheless, the Freundlich Isotherm curve, or even one point on it, is a useful criterion for the screening of adsorbents. However, the widespread use of the technique of Freundlich is in itself an indication that rarely can investigators expect to effect complete removal of solutes from solution via batch treatments. Rather, these treatments are useful for comparison purposes in examining more than one agent.

As previously indicated, in conducting a few of these combination tests, the writers were concerned more with formulating an opinion concerning the prospects of massive organic substance removal from secondary sewage effluent via batch procedures, than with comparing the results of the treatments. The tests were conducted on unfiltered Mt. Holly secondary sewage effluent and the treated effluents were filtered through E & D 615 paper. Milled rutile was included in these treatments as a source of tetravalent titanium. $TiCl_4$ had exhibited an affinity for some of the organic refractories in sewage when precipitated, as TiO_2, in the effluent. The treatments and the results of each treatment are recorded in Table 19.

Hydrogen peroxide and powdered Ionac A-540 ion exchange resin (chloride form) were employed in other combination batch tests. In these tests, the secondary sewage was pre-filtered through Whatman #5 paper. One portion was treated with H_2O_2 only, while another portion was treated with the A-540 only. Other portions were treated with H_2O_2 followed by treatment with A-540. The tests were of the usual jar-type variety (with 50 minutes agitation, in contact with the resin, at 50 RPM). Higher residual C.O.D. values were noted on sewage where the dual treatment was employed, than on sewage which was treated with the Ionac A-540 resin powder alone. The results of these tests are summarized as follows:

Table 5

Batch Treatments Employing H_2O_2 and Ionac A-540 Ion Exchange Resin (Cl^- form)

Initial C.O.D. of Sewage, Mg/l.	PPM H_2O_2 Added	H_2O_2 Contact Time Before Resin Treatment	PPM Resin	Residual C.O.D., Mg/l.
115	None	None	555	58
115	10	10 Minutes	None	121
115	10	10 Minutes	555	75
115	10	100 Minutes	500	65

3.3 Columnar Bed Testing

The use of columnar beds was included in these studies primarily for testing of some insoluble polymeric substances. A batch treatment of secondary sewage, as previously discussed, cannot be expected to remove all refractory substances. Such batch treatments, therefore, provide the investigator with no specific knowledge of the versatility of a substance, that is, the affinity of a given substance for all or most of the refractory contaminants as opposed to an affinity for only one or two. Granted, there are some who may feel that an adsorbent, or other agent, which is specific for only one or two solutes, when placed in a medium with many, is indeed a versatile material. This study is, however, concerned primarily with massive refractory contaminant removal. Columnar bed treatments, while relatively more time consuming than batch treatments, readily tell whether or not a substance is capable of lowering the C.O.D. of a secondary sewage effluent to zero.

The flow rate in testing of most columnar bed materials was 10 ml. of effluent per two minutes.

3.3.1 Ion Exchange Resins

3.3.1.1 Ionac A-300 and Ionac A-540

Two resin beds were set up in glass tubes having sintered glass discs to support the resin. The inside diameter of these tubes was 23.5 mm. One bed consisted of 10.00 grams (dry weight) of Ionac A-300 (a granular, medium base anion exchanger), and had a bed-volume of 29.7 ml. after soaking and washing with demineralized water. The other bed consisted of 10.00 grams (damp, swollen weight; 5.17 grams dry weight) of Ionac A-540 (a bead-type, strong base anion exchanger), and had a bed-volume of 16.95 ml. Both resins were in the chloride form. Filtered Mt. Holly sewage effluent was passed through each. C.O.D. and chloride tests were run on the effluent after passage through the beds. (The sewage effluent was passed through each bed at the rate of about 10 ml. every 2 minutes). The results of these tests, versus the volume of effluent passed through each bed, are summarized in Figs. 10 & 11. The increase in C.O.D. and chloride content during the passage of the first 1000 ml. of effluent through the Ionac A-540 resin bed may be attributed to the fact that newly synthesized ion exchange resins often have a tendency to leach impurities when first placed into service. The break-through capacity of each of these resins appears to be about 100 bed volumes. However, considerably more effluent than that was passed through each. After the passage of the effluent, through the beds, attempts were made to regenerate the resins to their original capacities with warm (60°C.) 10% NaCl solution followed by warm 10% NaOH and then again by 10% NaCl. The A-300 was regenerated to about 14% of its original capacity, while the A-540 was regenerated to about 46% of its original capacity. This fouling might have been reduced if regeneration had been attempted sooner. From the data observed from these two runs, other synthetic ion exchange resins were considered with regeneration following the passage of 100 bed-volumes through the bed.

3.3.1.2 Ionac A-260

A 17.4 ml. bed of Ionac A-260 (granular, weak base anion exchanger) containing 5.0 gm. of the resin (dry basis) was set up in a glass tube with a sintered glass bottom. Pre-filtered secondary sewage effluent was then passed through this bed. After 20 bed volumes had passed through, the effluent so treated had dropped in C.O.D. by 40 mg/l. After 100 bed volumes, the drop in C.O.D. was only 16 mg/l. Attempts to regenerate this resin with NaCl and NaOH failed.

3.3.1.3 Ionac XLA-400

Two columnar beds of "Ionac XLA-400" (a bead-type, strong base anion exchanger) were employed in testing the ability of this resin to remove refractory substances from sewage. Each bed had a depth of 35 mm. and a diameter of 23.5 mm. (or a bed volume of 15.17 ml.). The sewage was passed through the beds at a rate of 10 ml. every 2 minutes. Bed #1 was initially eluted with a 10% aqueous NaCl solution to assure maximum chloride conversion, and regenerated after each succeeding 100 bed volumes, by successive treatment with aqueous solutions of 10% NaCl, 10% NaOH, and 10% NaCl. Bed #2 was also initially eluted with 10% NaCl solution, but was regenerated after 100 bed volumes with 10% NaCl followed by 0.5% aqueous NaOCl. Each bed was rinsed thoroughly with demineralized water following each regeneration treatment (to remove excess NaCl, NaOH, or NaOCl). The OH^- exchanged by the resin (of Bed #1) was quantitatively measured following its displacement by Cl^-. This test provided some measure of the regenerability of the resin in this bed.

Resin Bed #1

A total of 5047 ml. of filtered sewage effluent, the C.O.D. of which varied from 72 mg/l. to 137 mg/l., was passed through this bed. Regeneration was attempted twice; after passage of 1766 ml., and 3427 ml. of the effluent through the bed. The residual C.O.D. of the effluent, after passing through the column, varied from 25 mg/l. to 82 mg/l. The drop in C.O.D. of the effluent, after passing through the column, varied from 41 mg/l. to 62 mg/l. The chloride correction of the effluent, after passing through the column, remained fairly constant varying from 37 mg/l.

to 44 mg/l. The constancy of the chloride corrections is an indication that the resin was being successfully regenerated. Further indication that the resin was successfully being regenerated was found in the OH^- capacity of the resin following treatment with 10% NaCl. After the first regeneration, the bed had a capacity of 15.85 meq. of NaOH, and after the second regeneration, had a capacity of 15.55 meq. of NaOH.

Resin Bed #2

A total of 3156 ml. of filtered sewage effluent, varying in C.O.D. from 72 to 137 mg/l., was passed through this bed. This bed was regenerated following passage of 1646 ml. of effluent through it. A comparison of the performance of Beds 1 and 2 is shown in Table 6 below.

Table 6

Sewage Treatment Employing 15 Ml. Beds of Ionac XLA-400

Quantity of Sewage Passed Through Bed (in Bed Volumes)		Influent COD Mg/l.	Effluent COD Mg/l.		Drop in COD After Passing Through Bed, Mg/l.	
Bed #1	Bed #2		Bed #1	Bed #2	Bed #1	Bed #2
21.4	----	94	50	—	44	—
102	----	87	25	—	62	—
116	0	Regenerated				
137	22.1	72	31	32	41	40
236	98.2	72	30	25	42	47
236	108	Regenerated				
343	198	137	82	59	55	78

Ionac "XLA-400" Resin (Chloride Form) 95 Ml. Bed

In an effort to increase the drop in C.O.D. of secondary sewage effluent on passing through NaCl regenerated "Ionac XLA-400" resin, a larger bed was set-up. It was felt that the drop in C.O.D. might be increased by employing a larger bed, thereby increasing contact time and minimizing the effects of "channelling". Accordingly, a bed with a depth of 251 mm. and a diameter of 22 mm. (or a bed volume of 95 ml.) was tried.

The initial C.O.D. of the effluents passed through this bed varied from 99 mg/l. to 125 mg/l.

The results of the testing done on this bed are summarized in the following Table:

Table 7

Sewage Treatment Employing a 95 Ml. Bed of Ionac XLA-400

Quantity of Effluent passed through bed (in Bed Volumes)	Influent C.O.D.	Effluent C.O.D.	Drop in C.O.D. after passing through Bed (in mg/l.)
3.63	99	28	71
6.63	125	24	101
15.08	122	52	70
21.83	122	41	81
31.58	117	49	68

When the above values are compared with the drop in C.O.D. experienced with the smaller column (Bed #1, chloride form), the results indicate that the column efficiency can be increased markedly, at least for the number of bed volumes reported above, by the use of a longer column of resin.

It is interesting to note that the properties of this resin can be modified according to degrees of crosslinking. These tests indicate that this resin is regenerable after the passage of sewage through it, in spite of the fact that such a condition is conducive to fouling. A sufficient number of cycles, however, was not recorded to establish that this resin would be an economical agent for refractory contaminant removal from secondary sewage effluent. Should regeneration problems occur after several cycles, the ability to vary the degree of cross-linking within this resin might effect a solution to such problems.

3.3.1.4 Ionac C-270 and C-240 (H^+ forms)

Two commercial cation exchange resins were employed in columnar bed testing procedures. These resins were considered in this study primarily in the testing of Rosin Amine D, where they were tried for removal of Rosin Amine D from aqueous media.

Ionac C-270 (weak acid) and C-240 (strong acid) were used in these tests. Both were in the H^+ form. 300 ml. of a 50 ppm aqueous solution of Rosin Amine D were passed through a 15 ml. bed of each of these resins. Prior to passage through the beds, the Rosin Amine D solution exhibited a C.O.D. of 154 mg/l., and readily formed a precipitate on the addition of a few drops of sulfuric acid. After passage through the column of Ionac C-270, this Rosin Amine D solution had been lowered in C.O.D. to 18 mg/l. When passed through the Ionac C-240 bed, the C.O.D. of the formerly 50 ppm Rosin Amine D solution had dropped to 9 mg/l. The eluted liquor from each column was again tested with a few drops of sulfuric acid, and no precipitate was formed. No further testing was done on Ionac C-270 during this study.

Tests were run, employing Ionac C-240 (H^+ form) to further study the effect of Rosin Amine D on pre-filtered (Whatman #5 paper) secondary sewage effluent, and the effect of the Ionac C-240 on the sewage effluent. Initial testing of this amine in batches had produced a treated effluent with a C.O.D. somewhat higher than the untreated effluent. Filtered Mt. Holly sewage, with a C.O.D. of 100 mg/l. was employed in these tests.

Five-hundred ml. of the sewage effluent were treated with 50 ppm of Rosin Amine D, then filtered. One percent diatomite was employed in the filtration, as in the case of the batch tests, to effect reasonable clarification of the effluent following the amine treatment. Three hundred ml. of the amine treated, diatomite filtered effluent was passed through a 15 ml. bed of Ionac C-240 resin. The C.O.D. of the eluted effluent was 48 mg/l.

A second 15 ml. bed of the Ionac C-240 resin was used to treat 300 ml. of the pre-filtered secondary sewage effluent having a C.O.D. of 100 mg/l. This sewage aliquot was pretreated only with a 1% diatomite filtration. The effluent, after passing through the Ionac C-240 bed, had a C.O.D. of 66 mg/l. The use of Rosin Amine D, in the indicated sequence of treatments, does not appear promising. The C.O.D. lowering effect on the effluent, which could be attributed to 50 ppm of Rosin Amine D, was only 12 mg/l.

3.3.2 Proteinaceous Substances

A few proteinaceous materials were tried, without modification, in attempts to lower the C.O.D. of secondary sewage effluent. Prefiltered secondary sewage effluent was passed through a bed of a 40% gluten feed supplement, a bed of casein, and a bed of soya protein. In an effort to prevent dispersion of the protein, the pH of the effluents passed through the casein and soya protein beds were pre-adjusted. Preliminary attempts were made to prevent agglomeration of proteins by mixing them with sand. No success was registered with the sand-protein mixture.

3.2.2.1 Forty Percent Gluten Feed Supplement

A bed of 40% gluten feed supplement was prepared. This bed was pre-rinsed with demineralized water until no further color was imparted to the rinse water. Pre-filtered sewage effluent was then passed through the column. The C.O.D. of the sewage was greatly increased after passing through this column. A 50 ml. aliquot of the eluted effluent consumed all of the dichromate in the course of the reflux period. A coagulation treatment of the eluted effluent, employing 60 ppm $FeCl_3$ was tried. This post-treatment failed to lower the C.O.D. to a point where a 50 ml. aliquot would not reduce all of the dichromate in the quantitative C.O.D. test.

3.2.2.2 Casein and Soya Protein

Columnar beds of both casein and soya protein were tried during this study. Pre-adjustment of the pH of the sewage to 3.0 with HCl, prior to passage through these beds, was employed in an effort to prevent agglomeration and leaching. No success was attained via this technique.

3.3.3 Modified Proteinaceous Substances(191, 223)*

Various attempts were made to modify proteins so that they could be tested in bed form. Modification treatments were tried wherein proteins were 1) dispersed in NaOH solution, then reacted with a ferric compound; 2) reacted with a ferric compound in the granular undispersed state; 3) reacted with formaldehyde in the undispersed state; 4) reacted with formaldehyde in the undispersed state, then with a ferric compound, an acid, an acid salt, or a base and 5) reacted with formaldehyde in the dispersed state, then with a ferric compound.

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* A copy of U.S. Pat. 2,393,269(191) is in Appendix C of this report.

During the quest for suitable proteins and modification techniques, two groups of rather elementary tests were set-up employing zein and casein compounds. The tests were intended to furnish information to be used in coping with the problem of leaching. One group consisted of proteinaceous substances in contact with sewage effluent for 65 hours. The other group also consisted of proteinaceous substances in contact with sewage effluent for 65 hours, but the pH of the sewage was pre-adjusted to 3.0 with 1:1 HCl. None of the proteinaceous substances imparted any noteworthy immediate changes in the appearance or odor of the supernatant sewage. The appearance and odor of each mixture was noted again after the contact period. The results of these tests are tabulated below:

Table 8

Some Effects of Sewage on Casein and Zein, as Modified.

Filtered Sewage with No Pre-Adjustment of pH

Proteinaceous Substance	Observations after 65 Hours Contact Time
1. None (control)	Typical appearance and odor.
2. Undispersed zein treated with $FeCl_3$	No change in appearance. Odor of protein is noticeable.
3. Casein treated with NaCl and formaldehyde	No change in appearance. Very slight odor of sewage-not as strong as control.
4. Zein treated with NaCl, formaldehyde, and H_2SO_4	Somewhat cloudy on shaking. Slight odor of protein.
5. Zein alone	Clear on shaking. Rather strong protein odor. Slight putrid odor also detected.

Filtered Sewage with pH Pre-Adjusted to 3.0

Proteinaceous Substance	Observations after 65 Hours Contact Time
1. None (control)	Typical appearance and odor (unchanged by adjustment of pH).
2. Undispersed casein treated with $FeCl_3$	No change in appearance. Odor of protein is noticeable.

Filtered Sewage with pH Pre-Adjusted to 3.0 -continued-

Proteinaceous Substance	Observations after 65 Hours Contact Time
3. Casein treated with NaCl and formaldehyde	No change in appearance. Very slight odor of sewage-not as strong as control.
4. Zein treated with NaCl, formaldehyde, and H_2SO_4	Clear on shaking. Very slight protein and sewage odors.
5. Zein alone	Cloudy on shaking. Strong putrid odor.

3.3.3.1 Reaction of Dispersed Proteins with Ferric Compounds

Of the proteins which were dispersed in caustic, then precipitated with a ferric compound, only casein showed promise. The other materials (Permutit 65 gelatin, Swift's "Fluid 69", Swift's "4V" and ADM Soya Protein "Adpro 112 B") when dispersed in 2% NaOH on the weight of the protein, and precipitated with 10% $FeCl_3$ on the weight of the protein, were not amenable to bed testing procedures.

Similarly dispersed casein was reacted with $Fe_2(SO_4)_3$. The resulting curds were mixed with washed sand and the mixture tested as a bed material. Prefiltered secondary sewage effluent readily passed through this bed at a relatively unrestricted flow rate. Prior to passage through the bed, the sewage had a C.O.D. of 110 mg/l. After passing through the bed, a portion of the sewage was reduced in C.O.D. to 76 mg/l. A post-coagulation of the same sewage passed through this bed, employing 60 ppm $Fe_2(SO_4)_3$, calculated as $FeCl_3$, further lowered the C.O.D. to 57 mg/l. The additional drop in C.O.D. was believed due to the coagulation of protein, which had leached from the curdy casein precipitate.

3.3.3.2 Reaction of Undispersed Proteins with Ferric Compounds

Several undispersed proteinaceous substances, when reacted with ferric chloride or ferric sulfate, were employed in these studies. Casein, 40% gluten feed supplement, food grade (70%) gluten, soya protein, and various glues and gelatins were reacted with ferric chloride. The resulting glue and gelatin compounds exhibited no stability to speak of when in contact with water or sewage. Eventually all of these compounds were abandoned after various stages of testing, due to their leaching of organic substances, even when 20 ppm of NaOCl is added to the effluent to control microbes.

The less hydrophilic of these compounds, notably the 40% gluten feed reacted with $FeCl_3$, proved to have an affinity for A.B.S., however. A test was run on a columnar bed of this compound, employing a synthetic laundramat effluent containing 60 ppm A.B.S. The material used in this test was prepared as follows:

> 30.0 g. of 40% gluten feed supplement (G.L.F.) was reacted with an excess of $FeCl_3$. The material was rinsed twice during which time 3.9 g. (dry basis) of fine material was removed and discarded. It is estimated that the feed will react with approximately 4% of its weight in $FeCl_3$.

The results of the analysis of the effluent after passing through this bed are shown in Table 9 below.

Table 9

Effect of a Gluten Feed-$FeCl_3$ Compound on the A.B.S. in Synthetic Laundramat Effluent containing 60 ppm A.B.S.

Volume of Effluent Passed Through Bed, Ml. (Cumulative)	ABS Content of Effluent Passed Through Column, PPM
800	NONE FOUND
3100	2.5
3800	3.6
4750	4.8
9000	13.6*

* Composite of final 4250 ml. passed through column

3.3.3.3 Reaction of Proteins with Formaldehyde(223)

Granular undispersed casein was reacted with formaldehyde. Thirty-four grams of casein was placed in a solution consisting of 54 g. of NaCl, 60 ml. of 37% formaldehyde, and 400 ml. of demineralized water. The mixture was held at 60°C. for 15 minutes, with occasional stirring, then the supernatant solution was decanted and the treated casein was washed free of NaCl and formaldehyde. It is believed that the NaCl-formaldehyde solution can be reused several times to "harden" proteins.

An attempt was made to repeat the procedure with 50 grams of zein. The zein coagulated into a single, sticky, elastic lump. This lump was hardened by addition of 10 ml. of concentrated H_2SO_4 to the bath solution followed by oven-drying at 100°C. Air was squeezed out of the lump during the sulfuric acid treatment to allow penetration of H_2SO_4. Due to the questionable uniformity of this material, it was not used to test for its capacity to remove refractory substances from sewage. No further attempt was made to devise a method for obtaining a uniformly cross-linked and hardened zein product, due to the cost of zein as compared to the cost of casein.

The same procedure employed to harden casein via NaCl and formaldehyde was also successfully employed to harden a relatively cheap livestock feed mixture containing 40% corn gluten protein.

The protein-formaldehyde compound proved to have no affinity for the organic refractory substances present in sewage. The casein-formaldehyde compound, however, proved capable of separating metal salts in an aqueous mixture. Color bands, characteristic of the color imparted by certain cobalt, iron, chromium, and copper salts appeared in a bed of casein-formaldehyde compound when a mixture of these salts was eluted through that bed.

Further reaction of the casein-formaldehyde compound with ferric compounds showed much promise for removal of refractories from sewage. As a result, the formulation and testing of many variations of protein-formaldehyde-acid and acid salt compounds was given much attention during this study.

A hypothesis was proposed to account for the failure of the formaldehyde treated casein, per se, to remove any organic matter from the water and the ability of the protein to do so following contact with strong ferric chloride or ferric sulfate solutions. We believe the mechanism to consist of

1. low pH of the iron salt solution promotes hydrolysis of methylol groups which block the amino exchange sites

on the protein.

2. low pH also promotes the splitting of inner salt bridges (the so-called zwitterion), thus exposing more amino exchange sites.

Partial corroboration of this hypothesis was obtained when the formaldehyde treated casein was exposed for some hours to hydrochloric acid. Thus from a sample of Mt. Holly secondary effluent which disclosed a C.O.D. of 107.7 mg/l., passage through a bed of casein-formaldehyde-hydrochloride lowered this to 30.7 mg/l. at the seven bed-volume point. The eluate was moderately strongly acidic (2.5-3.5 pH) and ran high in chloride. Less successful were sulfuric and phosphoric acids. The latter was to have the additional virtue of easy phosphate removal per calcite bed.

The lime treatment of the formaldehyde protein was based on the premise that sufficient hydrolysis of zwitterion and methylol groups could be induced to completely dispense with chloride. The results indicate that a severe leaching of protein takes place so that the eluate displayed a somewhat higher C.O.D. than the raw influent.

3.3.3.4 Reaction of Undispersed and Dispersed Protein with Formaldehyde plus Various Other Compounds

Granulated, undispersed casein was reacted with formaldehyde, then with an excess of ferric chloride. This material was employed as a bed for testing its effect on the refractory substances in secondary sewage effluent.

This bed had a depth of about 78 mm. and a volume of about 30 ml. Filtered sewage effluent was passed through this bed until it no longer lowered the C.O.D. of the effluent. The following Table summarizes the results of the passage of the effluent through this bed:

Table 10A

Treatment of Secondary Sewage Effluent with a Casein-Formaldehyde-$FeCl_3$ Compound

Quantity of Sewage passed through bed (in bed volumes)	Initial C.O.D. of Sewage Effluent Mg/L.	C.O.D. of Effluent after Passing Through Bed, Mg/L.	Drop in C.O.D. Mg/L.
5.87	105	45	60
15.80	105	60	45
29.80	100	97	3

Following exhaustion with secondary sewage effluent, this bed was regenerated as follows:

1) The Fe^{+++} was first eluted with 40 ml. of 9% HCl solution, then the excess HCl was washed out with demineralized water.
2) The adsorbed organic substances, apparently now more loosely bound in or on the casein compound in the absence of Fe^{+++}, were eluted with 100 ml. of 9% NH_3. The excess NH_3 was then washed out with demineralized water.
3) Passed 6% $FeCl_3$ through bed of casein compound until original volume and color were returned.

Following regeneration, a 60 ppm solution of standard A.B.S. was passed through the bed. The regenerated bed successfully removed all A.B.S. from the solution. More than 11 bed-volumes of the solution were passed through the bed.

Another bed, with the same depth and volume as the casein compound described above, was set up. This bed consisted of a formaldehyde-hardened livestock feed mixture (40% corn gluten) reacted with an excess of $FeCl_3$. After about 15 bed volumes of 60 ppm A.B.S. solution were passed through the bed, the effluent was still being lowered to less than 0.1 ppm A.B.S.

Leaching of C.O.D. imparting organic substances by this feed-formaldehyde-$FeCl_3$ compound impeded the evaluation of its effect on sewage. Another bed of this material was set-up, however, to learn what effect it would have on the color bodies present in Rancocas Creek water. Much of this coloring matter is believed due to humates and humic acids; similar substances being present in sewage.

The creek water was first filtered through Whatman #5 paper, and then passed through the column. While this test was not intended to be quantitative, it indicated that the bed material will remove much of the material responsible for imparting color to the creek water.

Two more beds of casein-formaldehyde-$FeCl_3$ compound were set-up. Filtered Mt. Holly sewage was passed through one, and filtered Camden sewage was passed through the other.

Both columns were exhausted after approximately 43 bed-volumes had passed through. The initial C.O.D. of each effluent was similar (Mt. Holly = 80-86 mg/l., Camden = 69-80 mg/l.). The sewage passed through each column was lowered similarly in C.O.D. (Mt. Holly by 6-43 mg/l., Camden by 11-38 mg/l.), also the apparent greater capacity of the casein-formaldehyde-$FeCl_3$ compound for C.O.D.-imparting substances in these examples (as evidenced by the 43 bed-volumes) as compared to the example given above (29.8 bed-volumes) is probably due to two factors. One, of course, is the difference in C.O.D. of the original effluents (69-86 versus 100 to 105). The other is in the formulation of the compound. Longer contact times with formaldehyde and $FeCl_3$ seem to enhance the affinity of the casein compound for the refractory substances, and the compound used in the two beds to compare Mt. Holly and Camden effluents had longer reaction times. The contact time with formaldehyde was one hour and 15 minutes at 60°C. versus the usual 15 minutes at 60°C. The contact time with $FeCl_3$ was 4 hours versus the usual 1-2 hours.

Table 10B

Comparison of Mt. Holly vs. Camden Secondary Sewage Effluents. Columnar Bed Treatments with Casein-Formaldehyde-$FeCl_3$ Compound

Mt. Holly Effluent				Camden Effluent			
Bed Volumes	Initial C.O.D. Mg/l.	C.O.D. After Treatment Mg/l.	C.O.D. Lowering Effect Mg./l.	Bed Volumes	Initial C.O.D. Mg/l.	C.O.D. After Treatment Mg/l.	C.O.D. Lowering Effect Mg./l.
6.9	80	46	34	7.35	75	48	27
17.8	83	56	27	17.7	69	31	38
34.5	85	42	43	34.5	80	56	24
43.6	86	80	6	44.0	70	59	11

Formulating and testing of other casein-formaldehyde compounds was undertaken. The compounds, and their effect on sewage, as compared to casein-formaldehyde-$FeCl_3$ compound are summarized as follows:

Table 11

Comparison of Effects of some Modified Casein Compounds on Sewage Refractories

Casein-Formaldehyde	Capacity, Compared to Casein-Formaldehyde-$FeCl_3$
$-Fe_2(SO_4)_3$	Somewhat greater.
$-Al_2(SO_4)_3$	Removes organic substances, but results are not conclusive, since bed was not exhausted. Probably equal or less.
$-HCl$	Removes organic substances, but results are not conclusive, since bed was not exhausted. Probably greater.
$-H_3PO_4$	Less
$-H_2SO_4$	Less
$-Ca(OH)_2$	Less

Several other formulations of the casein-formaldehyde compound with additional agents were prepared and tested in granular, in granular-semi-floc, and in floc forms to determine their effects on the refractory substances in secondary effluent. Emphasis was placed on the control of soluble by-products of the treatments.

These casein compounds were subjected to lengthy rinses with very large volumes of water and the rinse water tested to determine its C.O.D. This was done with a view toward pre-dissolving any soluble organic matter from the product prior to its use in treatment of sewage. Another possible source of leachable organic substances could come from microbial action on the casein compound. While the casein, when hardened with formaldehyde and treated with a ferric iron compound is by nature resistant to such attack, it is believed that as the material exchanges sewage refractory substances for acid components of the compound, local pH raising effects could permit bacterial action, simultaneous with exchange of refractory substances at other sites. Mt. Holly's secondary effluent is chlorinated as a safety measure to control pathogens owing to the limited size of the Rancocas Creek, into which the final effluent is ejected. This amount of residual chlorine may well be insufficient for the purpose of protecting the casein compound until exhausted.

Another way in which soluble substances are imparted into the treated effluent is by their exchange for the organic refractory substances in sewage. These soluble substances are inorganic acids. Which acid will be present is, of course, determined by the acid or acid salt component of the casein compound. H_3PO_4 can be removed via a calcite bed. The more promising forms of the casein compound, however, are the $FeCl_3$ form, the $Fe_2(SO_4)_3$ form, and the HCl form. Their use would necessitate the removal of relatively large quantities of HCl or H_2SO_4. We have estimated that Ionac A-260 resin can solve this problem. The cost of this additional treatment with A-260 will vary somewhat according to whether its use is for HCl or H_2SO_4 removal. The ultimate cost of the use of this resin will depend on the organic content of the effluent following treatment with the casein compound, due to the possibility of organic fouling. This phenomenon can probably be eliminated by a polishing step, wherein activated carbon might be employed. The possible use of this resin in a post-treatment, de-acidifying step will be discussed later in more detail.

The formulation and testing of casein-formaldehyde compound with additional agents, prepared to emphasize control of organic leaching, was as follows:

a) An attempt was made to eliminate the Cl^- ion from treated sewage by treating a casein-formaldehyde-iron chloride compound with calcium oxide (1 gram of CaO: 30 grams of casein compound) to displace Cl^- with OH^-. This proved unsatisfactory. This was followed by two attempts to achieve the desired result via NaOH. A 0.1N NaOH solution had very little effect, while a 10% NaOH solution displaced the Cl^-, but rendered the compound more prone to leaching of organic substances.

b) Another attempt to solve the Cl^- ion problem was made by trying to pick it up in a bed of casein-formaldehyde compound. The bed of casein-formaldehyde compound was used to post-treat sewage passed through a bed of casein-formaldehyde-hydrochloric acid compound. When the first bed became exhausted, the second bed was to have been activated by the HCl picked up during the treatment process. It was determined from this and other tests that casein-formaldehyde compounds have little or no affinity for HCl at the concentrations involved here. (238)

c) Casein was reacted with HCl, with $CaCl_2$, and with $Ca(OH)_2$. The resulting compounds each proved to be unsatisfactory. This was apparent when excessive foaming of the rinse water was noted. They were given the advantage of several water rinses, but still failed to be useful in the treatment of secondary sewage effluent. Additional chlorination of the sewage was tried, in the case of the casein-$Ca(OH)_2$ compound, but did not help. Casein-calcium hydroxide compound was prepared and hardened with formaldehyde. This substance also proved to be of no value in removing refractory substances from sewage.

d) A casein-formaldehyde-hydrochloric acid compound was treated with 3.5% NaOH solution, rinsed and retreated with 1.5% NaOH solution. The resulting compound was apparently relatively chloride-free. As in the case of the previously mentioned NaOH treatment of casein-formaldehyde-iron chloride compound, (a), above, the chloride was eliminated in the treated effluent. However, the compound was rendered more prone to the leaching of organic substances. The above formulation was repeated, using a 10% $NaHCO_3$ solution treatment followed by a 5% $NaHCO_3$ solution treatment in place of the NaOH treatments. Again the compound proved unsatisfactory, due to leaching of organics.

e) The leachable organic substances in the casein compounds are probably proteins or protein fragments which might be rendered insoluble and/or more stable if cross-linked with a larger molecule than formaldehyde. Dialdehyde starch was therefore used in one experiment to replace formaldehyde. While this formulation removed refractory substances from secondary sewage effluent, it apparently did not offer a solution to the problem. The cross-linking agent represents a relatively small portion of the cost of modified casein compound, so more expensive agents can be considered for this purpose. This is particularly true if they are more efficient than formaldehyde, which forms several condensation products with casein other than the desired inter-molecular cross-linked product. These products must then be hydrolyzed by water-rinsing.

f) Casein dispersed in NaOH solution (0.5% NaOH on the weight of the casein) was precipitated with hydrochloric acid in the form of a floc, then reacted with formaldehyde, then with iron chloride. The purpose here was to try to eliminate leachable substances during reprecipitation of the casein and also to increase capacity for refractories by increasing the surface area of the compound. This material was also given the advantage of lengthy rinses with water. When compared to casein-formaldehyde-iron chloride compound on a weight basis, this compound appears to be of a superior capacity for refractory substances. However, it is not so stable to the effects of microbes when allowed to stand for a period of several hours.

g) Water soaking of casein, prior to reaction with formaldehyde and iron chloride, was tried as an alternative to reprecipitation of the casein for pre-removal of soluble organic substances. One-hundred grams of casein was soaked in one liter of water at room temperature for two hours. Medium agitation was maintained during this period (at a rate which was not so slow as to permit aggregating of the semi-solid casein granules, nor fast enough to effect complete solution of the granules). Following two rinses of the casein, during which great losses occurred, the soft granules were reacted with formaldehyde, then with ferric chloride. The resulting compound was rinsed with two liters of water. Tests of the material for leaching and affinity for sewage refractory substances were encouraging, but the dissolution of the casein in pre-soaking results in too great a loss for the process to be economical, unless the casein so dissolved or dispersed could be used for another purpose.

3.3.4 Inorganic Materials and Treated Inorganic Materials

3.3.4.1 Calcined Diatomaceous Earth

A bed of a commercial granular form calcined diatomaceous earth was tried in an effort to remove refractory substances from filtered sewage. This material proved unsatisfactory. Bed testing of it was abandoned due to a progressive restriction of the flow rate, which occurred during testing.

3.3.4.2 Inorganic Substances Treated with Rosin Amine D Acetate

Rosin Amine D acetate solution (500 ppm) was used to treat Ionac C-100 (a synthetic zeolite), Hyflo Super-Cel (a diatomite), and Dicalites 416, 436, 4106, and 4156 (various particle size gradients of perlite).

Three-hundred ml. of filtered sewage was passed through a pre-rinsed 15 ml. bed of each of the treated Ionac C-190 and Hyflo Super-Cel, and discarded. An additional 70 ml. was eluted and tested for C.O.D. Initially, the C.O.D. of the pre-filtered sewage was 100 mg/l. After passing through the treated Ionac C-150 bed, the C.O.D. was 102 mg/l., and after passing through the treated Hyflo Super-Cel bed, the C.O.D. was 94 mg/l.

While treated perlite performed no better on sewage, this material removed the A.B.S. from a 60 ppm A.B.S. synthetic laundramat effluent.

3.3.5 Activated Carbon

A 190 ml. bed of Ionac P-50 granular activated carbon was employed as a post-treatment of pre-filtered secondary sewage effluent. The pre-treatment of the sewage was a batch coagulation, at pH 3.0, employing 75 ppm of gluten (food grade) and 45 ppm of $FeCl_3$. The pH adjustment was made with HCl.

The pre-filtered sewage used in this test had an initial C.O.D. of 98 mg/l. The gluten-$FeCl_3$ treatment lowered the C.O.D. to 64 mg/l. (a similar coagulation treatment employing 200 ppm gluten and 120 ppm $FeCl_3$ lowered the C.O.D. of a portion of the same initial sewage effluent to 51 mg/l. The C.O.D. of this treated sewage, employing the larger dosages, was not further lowered on neutralization to pH 6.5 with CaO). The coagulant treated sewage, now 64 mg/l. in C.O.D., was then passed through the carbon column. The first 400 ml. eluted was discarded. A C.O.D. test was run on the next 100 ml. eluted, and found to be zero. This eluant was approximately neutral in pH and no chlorides were present. This phenomenon may be due to a small mineral fraction present in the carbon and might not be an indication of serious competition between the HCl and organic matter for adsorption sites on and within the carbon granules.

A portion of the sewage, which was coagulated with 75 ppm gluten and 45 ppm $FeCl_3$ but not passed through the carbon column, was neutralized to pH 6.5 with CaO. The effluent's C.O.D., after this neutralization step, was further lowered from 64 mg/l. to 52 mg/l. In contemplating further post-treatment (of coagulated-carbon polished effluent) with Ionac A-260 to remove acid, this CaO neutralization step cannot be considered, however.

A second 190 ml. bed of Ionac P-50 granular activated carbon was employed to treat pre-filtered secondary sewage effluent. The initial C.O.D. of this pre-filtered sewage was 106 mg/l. The first 550 ml. eluted was discarded. 3,450 ml. more was passed through. The C.O.D. of this 3,450 ml. of eluted sewage was 41 mg/l.

A third 190 ml. column of Ionac P-50 granular activated carbon was again employed to test its affinity for the refractory substances in filtered secondary sewage effluent. The initial C.O.D. of the sewage used in this test was 100 mg/l. After passing 1,410 ml. through this bed, the C.O.D. of the eluted effluent was zero. The next 85 ml. eluted had a C.O.D. of 9 mg/l. After a total of 2,005 ml. of the effluent was eluted, an additional 250 ml. portion was eluted and tested for C.O.D. The C.O.D. of this last 250 ml. "cut" was 15 mg/l. The total volume of sewage eluted through this third carbon column was 2,255 ml.

3.4 Sludge Blanket Testing

A Spaulding type laboratory bench model precipitator was set-up (Fig. 2) and about 100 g. (dry basis) of a casein-$FeCl_3$ floc was placed in it. The casein-ferric chloride floc was prepared by dispersing casein in NaOH solution (0.5% NaOH on the weight of the casein), then adding the $FeCl_3$ as a 10% solution. This material was tested in a modified laboratory scale sludge-blanket apparatus. Thirty ppm of NaOCl was added to the sewage to afford additional protection of the bed. Since the floc is known to have an affinity for sewage refractories, this experiment was intended as a preliminary test to gain knowledge of the behavior of the floc under continuous upflow conditions involving some of the principles of the sludge-blanket apparatus. The material was not entirely satisfactory from this standpoint. Channelling was visually obvious, but was controlled by shaking the jug occasionally. This disturbed the floc bed sufficiently to require post-filtering of the effluent, since addition of clays at this point did not materially affect the settling properties of the solids. After about 4500 ml. of sewage had passed through the bed, the C.O.D. of the resulting effluent was lowered from 86 mg/l. to 38 mg/l.

The sludge blanket apparatus was modified, incorporating the basic design features of the Permutit Precipitator. It consisted of an agitator down through the stem of a long-stem inverted funnel which had been placed in a 4 l. beaker (as depicted in Figure 3). The effluent was passed downward through the stem and upward through the narrow, circular opening between the perimeter of the funnel and the side walls of the 4 l. beaker (close to the bottom of the beaker). The sludge blanket build-up takes place outside the funnel, and above the narrow, circular opening.

Sufficient agitation (at 160 RPM) in the lower zone of the beaker is in this way maintained to minimize channelling, through the sludge while permitting a clarified, floc-free quiescent upper zone. The addition of 30 ppm NaOCl to sewage used in sludge blanket treatment was continued.

The following "sludge blanket" treatments were done on filtered secondary sewage effluent in the inverted funnel apparatus:

Thirty ppm of NaOCl was added to all sewage effluent.

a) A casein-$FeCl_3$-formaldehyde floc (51 gm. dry basis) was prepared. Excess moisture was removed from the floc by vacuum filtration. The material was then placed in the apparatus and filtered sewage having an initial C.O.D. of 98 mg/l. was passed through it. Four thousand ml. was passed through the floc (to fill the beaker) then 1400 ml. additional volume was passed through and a sample then taken for a C.O.D. test. At this stage, the C.O.D. was 29 mg/l. lower than the influent sewage. Fourteen-hundred ml. more was passed through the sludge blanket, then a sample was again tested for C.O.D. The C.O.D. at this point was 26 mg/l. lower than the influent sewage.

b) An "in situ" precipitation of casein by an H_2SO_4-$Fe_2(SO_4)_3$ mixture was effected on a continuous basis in the sludge blanket apparatus. A total of 6 l. of filtered sewage having an initial C.O.D. of 98 mg/l. was treated in this manner with 50 ppm casein and 30 ppm $Fe_2(SO_4)_3$. 14.4 ml. of 5% H_2SO_4 and 0.38 gm. of $Fe_2(SO_4)_3$ (72%) were premixed with 600 ml. of the sewage. 0.33 g. of casein (90%) was dispersed in 0.1N NaOH solution and added to the remaining 5400 ml. of sewage. The mixtures were then blended in the sludge blanket apparatus, with the flow of the 5400 ml. of sewage containing casein regulated at approximately 10 times the flow rate of the 600 ml. of the sewage containing the acid and Fe^{+++} compound. The floc was permitted to build up as it formed. Following this treatment, the C.O.D. of the 6 l. of sewage had been lowered by 25 mg/l. The pH of the effluent so treated was lowered from 7.4 to 3.0.

c) The "in situ" precipitation of casein was repeated employing HCl and $FeCl_3$ in the place of H_2SO_4 and $Fe_2(SO_4)_3$. The same dosages (50 ppm casein and 30 ppm of the Fe^{+++} compound) were employed. This treatment lowered the C.O.D. of the filtered sewage (initially 87 mg/l.) by 29 mg/l. The pH of the sewage following this treatment was 3.3. An additional 60 ppm of $FeCl_3$, as a post treatment, followed by neutralization to pH 6.0 with CaO, did not further lower the C.O.D. of the sewage appreciably.

d) $TiCl_4$ was next tested in the sludge blanket apparatus. Here, a rapid mixing chamber was added to the apparatus to allow continuous feeding and mixing of the $TiCl_4$ and the sewage (as depicted in Figure 3). $TiCl_4$ is a fuming liquid which is difficult to handle and weigh. This problem was overcome by drawing a sufficient amount of the compound into a microburet via suction. The weight to be added was calculated as volume (in ml.) according to its specific gravity. The microburet was attached to a capillary tube which was fitted to a plastic bottle, the bottom of which had been removed. This bottle projected beneath the surface of the sewage with which the $TiCl_4$ was to be mixed. The $TiCl_4$ was fed dropwise, from the capillary tube, through the air-space within the bottle, into the swirling filtered sewage effluent, which initially had a C.O.D. of 89 mg/l. 140 ppm of $TiCl_4$ was employed on the weight of sewage. This treatment lowered the C.O.D. of the sewage by 40 mg/l.

e) Continuous coprecipitation of casein and $TiCl_4$ in the filtered sewage was also done in the sludge blanket apparatus. 50 ppm of casein was placed in the sewage and the sewage and $TiCl_4$ (140 ppm) were fed into the mixing chamber (as was the $TiCl_4$ and sewage in the previous run). The pH of the effluent so treated was lowered to 3.0 with HCl, then raised to 6.5 with CaO. This combination-treatment reduced the C.O.D. of the sewage (initially 121 mg/l.) by 49 mg/l.

3.5 Regeneration and Cost Estimate Studies

3.5.1 Cost Studies; Solid Adsorbents, Coagulants

Because of the marginal affinity of the ground minerals and industrial by-products for adsorbing organic substances from sewage, no emphasis was placed on a cost analysis of large-scale sewage treatments with these substances. Some may prove quite useful in treatment of some trade and other waste waters. Morris and Weber have found activated aluminum oxide to have an A.B.S. uptake of about one-third that of activated carbon. However, when these investigators extended these experiments to phenols and nitrochlorobenzenes, the results were not comparable to the results of their work on A.B.S. These investigators state that "It appears that this activated aluminum oxide does not have sufficiently broad adsorptive properties for general use, although it may be suitable for special treatment of detergent-bearing wastes."

Cost studies were undertaken for some coagulation techniques and the preparation of a modified, granular casein compound. Regeneration of the casein compound was undertaken to gain information on costs as indicated by the amount of regenerants used and the loss in affinity for organic sewage refractories following several regenerations (See 3.5.2, Page 71).

In batch treatments (as a coagulant), casein will remove from sewage a greater percentage of its weight in the oxygen equivalent of organic refractory substances than will activated carbon. Carbon, through 20 regeneration cycles, can be expected to remove slightly more than its own weight in the oxygen equivalent of refractory substances. Here, the cost of 20 regenerations must be added to the initial cost of the carbon. Casein (at 19¢/lb. versus about 15¢/lb. for activated carbon) should be more economical (if regenerated only a few times) than carbon, when employed in the sludge blanket continuous coagulation process. However, this process may not remove all of the refractory substances and a polishing step employing activated carbon may be required following the coagulation and sludge-blanket treatment.

The cost of materials fed into the precipitator would be 13.1¢/lb. This is based on current market figures for inedible casein, \$.19/lb., $FeCl_3$, \$.04/lb., NaOH, \$.03/lb. Dosages would be determined according to the organic content of the liquor to be treated. Table 12 lists some applicable dosages together with treatment costs without regeneration of the sludge.

Table 12

Raw Material Costs in Casein-$FeCl_3$ Coagulation Treatments of Secondary Sewage Effluent

Additives		\$/1000 Gallons
25 ppm Casein	15 ppm $FeCl_3$	\$.0446
50 ppm Casein	30 ppm $FeCl_3$	\$.0892
100 ppm Casein	60 ppm $FeCl_3$	\$.1784

The above Table includes the sodium hydroxide for the initial dispersion of the protein but omits the cost of prechlorination which would be required to inhibit microbial attack on the sludge blanket.

Considerably lower treatment costs can be realized if 70% gluten, food grade, at about \$0.08 per pound is substituted for the inedible casein, at about \$0.19 per pound. This will hold true even though in dispersing the gluten, somewhat more NaOH would be required.

Regeneration of the casein-$FeCl_3$ floc was not attempted. A dilute acid rinse should return this material to a form comparable to the raw casein used to prepare the original caustic dispersion, however.

It must be borne in mind, however, that the ferric compound (for example in any protein-$FeCl_3$ treatment) makes a major contribution to the removal of organic refractory substances. The additional cost of adding from 167 to 233% protein, on the weight of the ferric compound, may not be justified in all cases and with all sewage effluents (when comparing the drop in C.O.D. due to a protein-ferric compound coagulation with the drop in C.O.D. of a coagulation employing the ferric compound in the absence of protein).

In the lower dosages, for example 25 ppm of casein to 15 ppm of $FeCl_3$, the use of protein as a coagulant could prove quite useful due to proportionally greater synergistic effects at low dosage levels. In this dosage range, less Cl^- ion will be liberated also, and Cl^- ion must only be removed at additional expense in a post-treatment. The latter statement may not prove accurate, however, due to pH adjustments which must be made to effect coagulation (unless an acid such as H_3PO_4, which is readily removed via a calcite column can be substituted for HCl or H_2SO_4 in making these pH changes). That is, the pH of the mixture must be reduced to about 3.0 in the course of the coagulation, and $FeCl_3$ at the more modest dosage levels, will not in itself effect reduction of the pH to 3.0.

The cost of the sulfuric acid required to lower the pH of a mixture of 30 ppm $FeCl_3$, or $Fe_2(SO_4)_3$ calculated as $FeCl_3$, in secondary sewage effluent to 3.0 is approximately $0.02 per 1000 gallons. If hydrochloric acid is used instead of sulfuric, the cost will be $0.0372 per 1000 gallons.

Consideration of the cost of $FeCl_3$, $Fe_2(SO_4)_3$ and $TiCl_4$ to treat 1000 gallons of secondary sewage effluent is given in Table 13, below. The figures given below are the costs of the metal salts only.

Table 13

Cost of Some Metal Salt Coagulants in Treatment of 1000 Gallons of Secondary Sewage Effluent

Dosage PPM	$FeCl_3$	$Fe_2(SO_4)_3$*	$TiCl_4$
15	$0.005	$0.0026	
30	0.010	0.0052	
60	0.02	0.0104	
90	0.03	0.0156	
120	0.04	0.0208	
140			$0.2332

* Dosage calculated as $FeCl_3$. Requires heat or extended contact time to effect solution. Cost of heating is not included in these figures.

3.5.2 Cost Studies, Bed Materials

A bed-type compound of casein, formaldehyde, and ferric chloride was prepared for the purpose of material balance and cost estimate. The cost of the casein, formaldehyde, and ferric chloride required to make one pound of this material is 21.6¢, dry basis, allowing for losses in manufacture. This figure does not include the cost of sodium chloride (used as a catalyst in the formaldehyde treatment), or overhead costs of manufacture.

Studies of the feasibility of the regeneration of modified casein compounds indicated that this could be accomplished via a three step process, as indicated in section 3.3.3.4. In the case of a casein-formaldehyde-HCl compound, the elution of the Fe^{+++} (the first step) would be omitted.

A bed of casein-formaldehyde-ferric chloride compound was exhausted of its capacity for refractory substances in sewage. It was then stored at room temperature for two weeks, during which time the supernatent phase putrefied. It is believed that this was partly due to a leachable portion of the protein being imparted into the supernatent phase and there undergoing microbial decomposition, and partly due to attack on the protein compound itself (local pH effects would be neutralized on exhaustion, thereby permitting such microbial attack).

After the storage period, the bed was thoroughly rinsed, and regenerated six more times, during which no loss in bed volume was detected. No sewage was passed through the bed during these six regeneration cycles.

Following the regeneration series, 3.1 bed-volumes of filtered secondary sewage effluent (Mt. Holly) was passed through the bed. This effluent was then discarded and 0.6 bed-volume of the effluent through the column was collected and tested for C.O.D. and Cl^-. The net C.O.D. of the effluent (Cl^- corrected), prior to passage through the column, was 76.0 mg/l. After passage of a total of 3.7 bed-volumes of the sewage through the column, the net C.O.D. of the effluent was lowered to 16.9 mg/l; a drop of 59 mg/l.

The cost of regeneration solutions, exclusive of overhead costs of preparation and application of the solutions, would be approximately $1.00 per 1000 gallons of water treated. This figure is based on use of the solutions only once, for regeneration of a casein-formaldehyde-ferric chloride compound. It is likely that the solutions could be reused, however. In regeneration of a casein-formaldehyde-hydrochloric acid compound, the cost of regeneration solutions should be about one-third lower than the aforementioned figure, or about 67 cents per 1000 gallons. Again, this figure does not take into account the possible reuse of the regeneration solutions.

Most of the bed-type and coagulation treatments which have shown promise (by virtue of lowering the C.O.D. of Mt. Holly secondary sewage effluent) impart HCl or H_2SO_4 to the effluent. Ionac A-260 resin should offer a solution to this problem. This resin is prone to organic fouling, so it might be necessary for the residual organic substances (C.O.D. imparting refractories) to be removed before the treated sewage is passed through Ionac A-260.

It is quite conceivable, even likely, that the organic refractory substances removed via these coagulation bed treatments are of the larger molecular species. It is the larger species which are believed responsible for most organic fouling of ion exchange resins. Once removed, via the coagulation or bed treatment, the remaining organic substances may not foul the Ionac A-260 resin. A precoagulation might, for the same reason, also permit use of Ionac A-300 or Ionac A-540 resins without organic fouling.

The cost of deacidifying an organic-free effluent, or a non-resin-fouling effluent (containing 200 ppm of HCl) with Ionac A-260 is approximately $0.05 per 1000 gallons. If organic substances are present they must not, of course, compete with the acid for exchange sites. This figure is based on an effluent containing 200 ppm HCl because most of the treatments considered in this study would produce an effluent containing from 150 to 250 ppm of acid as HCl. This cost figure includes the resin plus soda ash for regenerating it, but does not include other overhead costs. Ionac A-260 resin costs $50.00 per cubic foot, as does Ionac A-300 resin. Ionac A-540 resin costs $58.00 per cubic foot. These prices are for lots of 400 cubic feet or more. No price data is available for Ionac XLA-400, since it is not currently in production, but it is expected that the cost of this resin would be in the $50.00 to $58.00 per cubic foot range.

4. DISCUSSION AND CONCLUSIONS

4.1 Adsorbents

No cheap, commercially available solid (such as a mineral or a manufacturer's by-product or scrap) is likely to remove all refractory substances as found in secondary sewage effluents, at least not so economically as does activated carbon. Such solids can be expected to make contributions to advanced waste treatment through removal of specific contaminants, however.

When employed in the sludge blanket apparatus, finely divided solid adsorbents such as clays and other minerals should have a mesh size of approximately 325. Such particles would be fine enough to expose a large surface area yet large enough that they would not be carried over into the clarified zone of treated effluent. If applied in the presence of the floc from a coagulation, however, a much finer particle size can be utilized.

Particle shape of solid substances appears to play only a minor role in adsorption affinity. The major factor is exposed surface area. Hydrous zirconia floc, for example, has many times the adsorptive capacity of dry, ground zirconium oxide.

4.2 Coagulants

Coagulation agents fed as liquids or in solution hold more promise than solid adsorbents in advanced waste treatment. Batch coagulations are not practical for waste treatment, such as tertiary sewage treatment, but continuous coagulation procedures such as the sludge blanket process should make substantial contributions to this field.

Lime, ferric chloride, and ferric sulfate, in conventional use now, should continue to contribute to waste treatment technology. These substances contribute inorganic anions to the treated effluents which must be disposed of lest they, too, build up in objectionable concentrations with reuse of the water.

Coagulation in the presence of most adsorption and ion exchange materials is technically feasible in the sludge blanket process for water treatment. Combining the specific properties of solid adsorbents and ion exchangers with those of coagulants might result in single tertiary treatments for the removal of residual or refractory substances from various secondary sewage effluents. Separating the components employed in such mixtures could be accomplished by differences in their settling characteristics. Regeneration of the components by the burning off of adsorbed contaminants, or other techniques, could then be accomplished. Such a process could be as cheap as, or cheaper than, treatments involving activated carbon.

The natural supply of minerals and other inorganic materials should not be considered to be endless, when contemplating their use for water treatment. The known occurrence of many minerals is confined to only limited geographical areas. From this standpoint, treatments involving organic products, such as carbons and proteins (which can be produced in a theoretically unending supply and in most geographic areas) would appear to hold an edge on mineral treatments. Suitable regeneration techniques, and cost factors in regeneration, could reverse this thinking, however.

4.3 Costs

The cost of tertiary treatments is difficult to define. Seasonal, even daily, variations occur in the number of contributing refractory species and in the proportions of these substances, one to the other. These variations can affect the cost of tertiary treatments. The writers have noted that the higher the C.O.D. of pre-filtered Mt. Holly secondary sewage effluent, the greater will be the drop in C.O.D. as a result of a given treatment.

5. RECOMMENDATIONS

As a result of our efforts and findings in the course of this study, the writers recommend attention be given to the following analytical procedures in the future:

a) Specific tests should be developed to analyze and correct for the presence of residual treatment agents present in treated effluents, where such residual agents interfere with the tests used to measure quality improvement due to a treatment. Such analyses would also be valuable in prescribing maximum treatment dosages.

b) More thought should be given to the standard pre-treatment (filtration through Whatman #5 paper) and pre-analyses of effluent prior to testing and post-treatment analysis with a view toward improving the reliability of the results of treatments involving different effluent samples obtained from the same source.

c) Techniques of infra-red and ultra-violet analysis should be included to obtain indices for the measurement of refractory contaminant concentration in sewage samples before and after treatment.

The writers further recommend that the following projects be included in the Advanced Waste Treatment Program of the United States Public Health Service:

a) Studies of coagulation techniques employing filtered versus unfiltered sewage effluents to ascertain whether the presence of the particulate matter will enhance adsorption of refractory substances; and to take advantage of these properties.

b) A study of quaternization of both hydrophilic and hydrophobic proteins to cheaply increase their affinity for organic refractory substances from waste waters.

c) A study of crosslinking of both hydrophilic and hydrophobic proteins to cheaply stabilize them for use in removal of refractory substances from waste waters.

d) A comprehensive study of the effects of selected solid adsorbents, as treated with selected chemical treatment solutions (such as salts of tetravalent metals; and mineral acids) on the refractory substances in secondary sewage effluents.

e) A study of the feasibility of employing electrolytic technology to regeneration of adsorbents.

f) A study of the acceleration of regeneration of solid adsorbents via ultrasonic excitation techniques(14), with emphasis on anionic refractory substances as adsorbed from waste effluents.

g) A study of regeneration of adsorbents and ion exchangers by the enzymatic action of bacteria and molds.

h) A study of the feasibility of selective breeding of bacterial and mold strains for degradation of troublesome organic materials.

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Archer-Daniels-Midland Company

Georgia-Pacific Chemical Company

Georgia Kaolin Company

Minerals and Chemicals Philipp Corporation

Hercules Powder Company

Shell Chemical Company
    Division of Shell Oil Company

California Products Corporation

Metal and Thermit Corporation

Floridin Company

Corn Products Company

John R. Borst, Inc.

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JNW:frs

APPENDIX A

Equipment Illustrations

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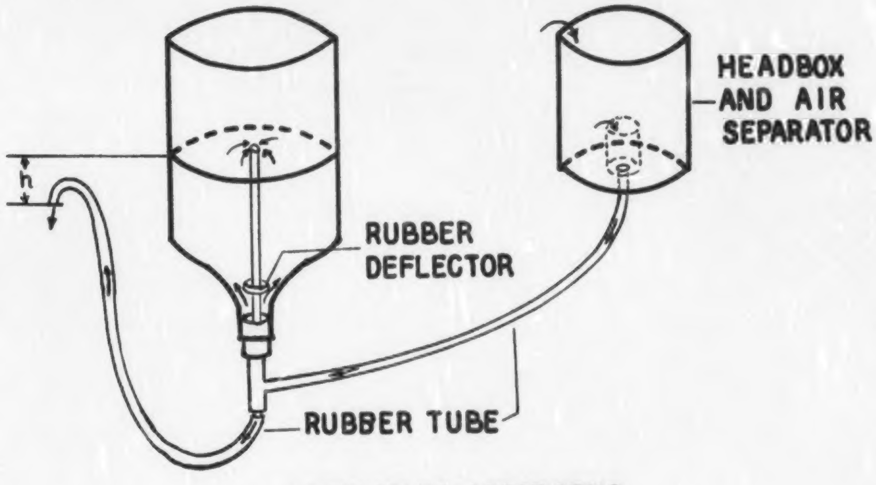
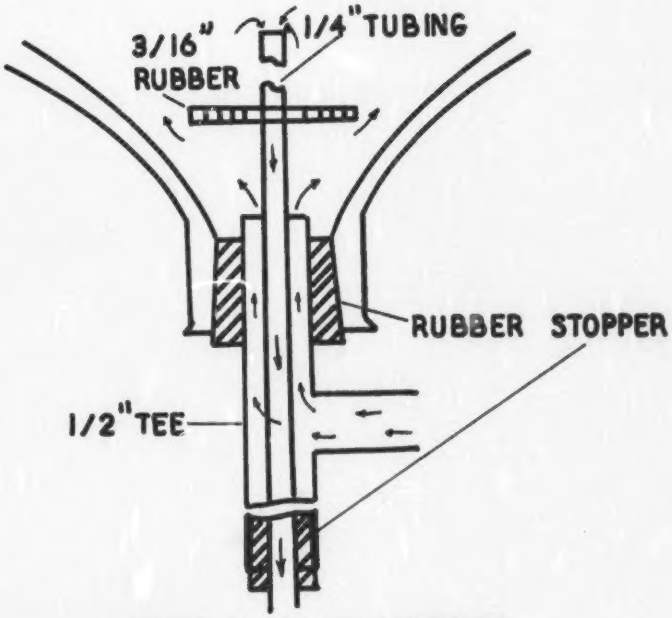
FIGURE 2 - SCHEMATIC DIAGRAM OF LABORATORY MODEL OF SPAULDING TYPE PRECIPITATOR
(C.CARPENTER AND C.C.PORTER, "WASTE WATER UTILIZATION BY CLARIFICATION," PROC.OF ANNUAL MEETING-TAPPI, N.Y.CITY, 1945)*


HEADBOX
AND AIR
SEPARATOR
h
RUBBER
DEFLECTOR
RUBBER TUBE

ASSEMBLED APPARATUS


1/4" TUBING
3/16"
RUBBER
RUBBER STOPPER
1/2" TEE

DETAIL OF INLET ASSEMBLY

* A COPY OF THIS PAPER IS IN APPENDIX C OF THIS REPORT

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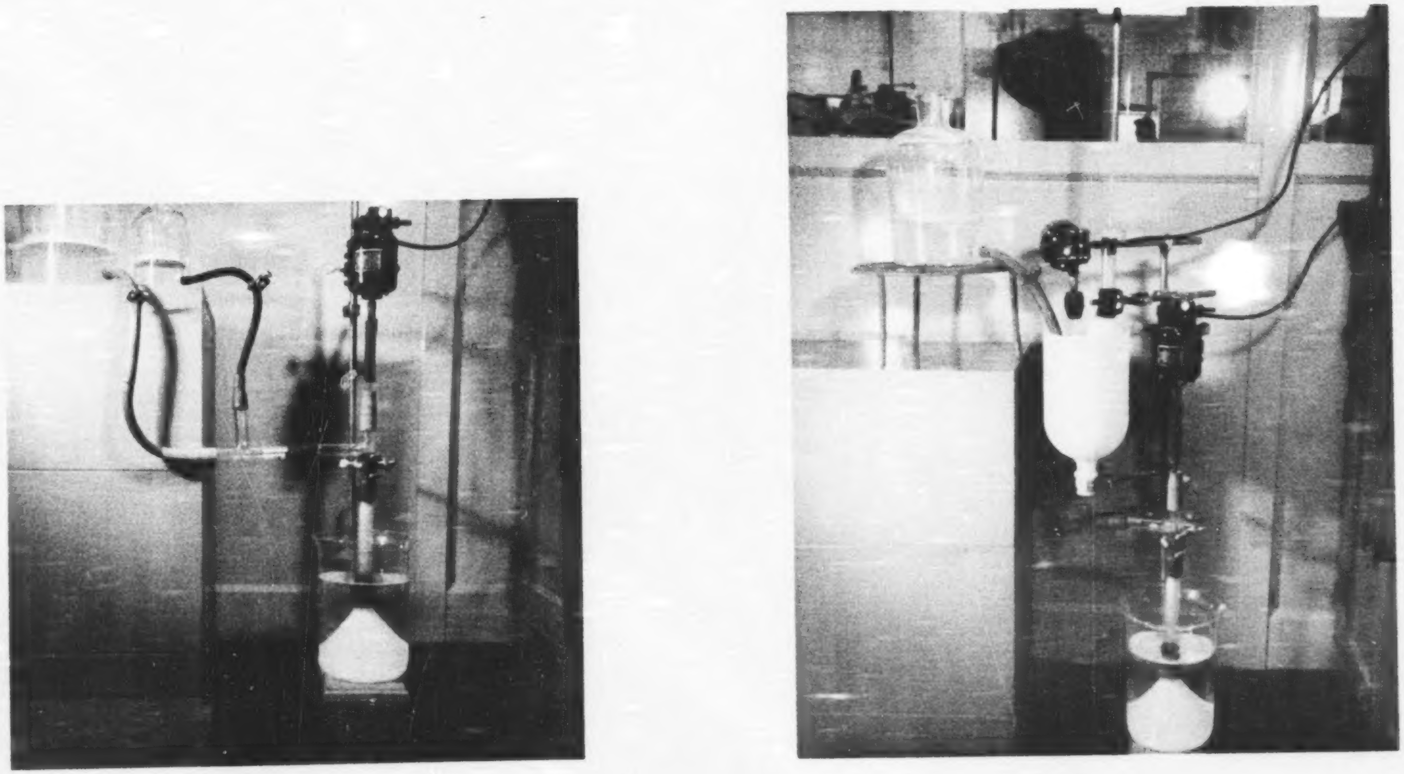
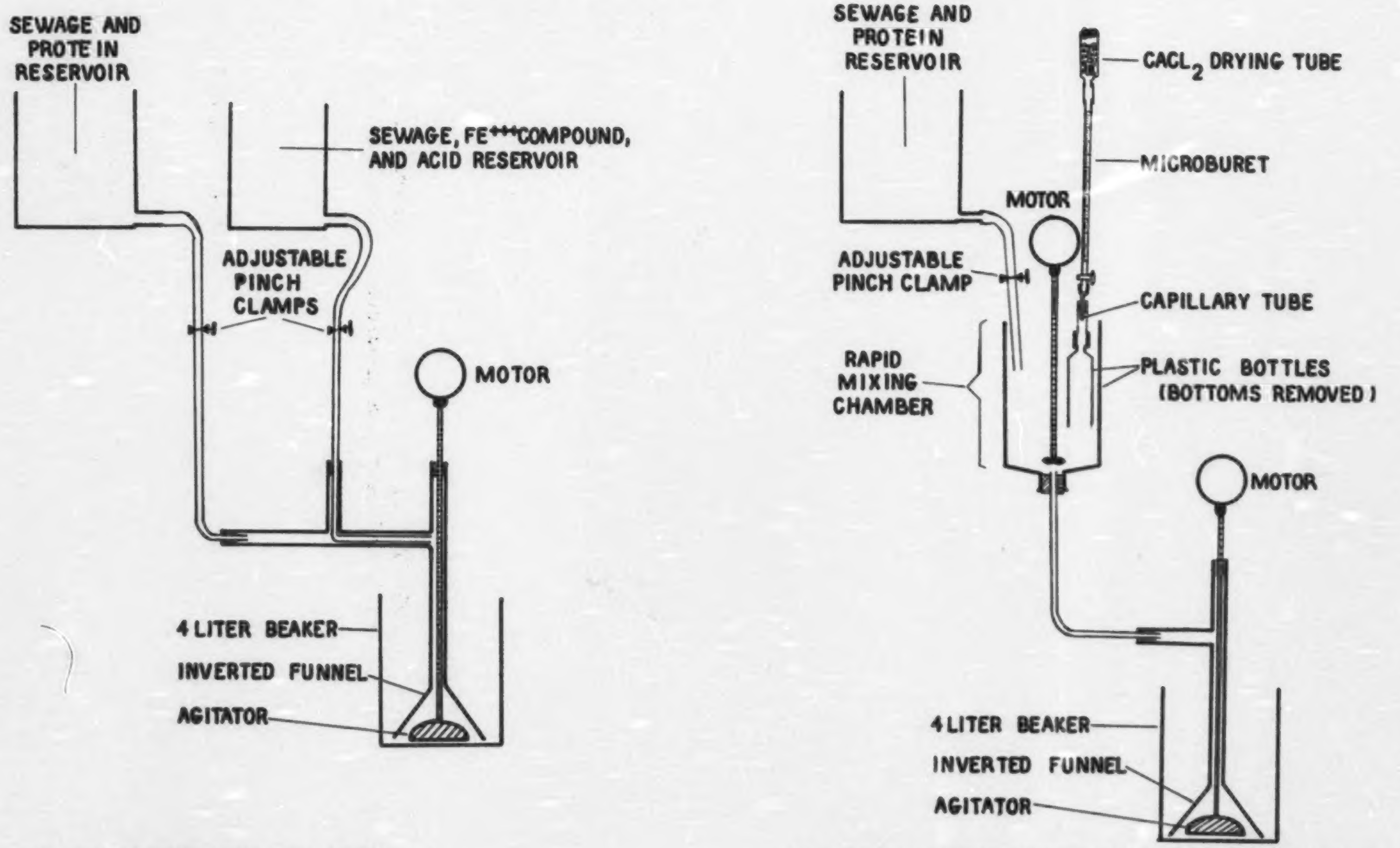
Figure 3. - Modified laboratory sludge blanket apparatus.



(A) Adapted for feeding of protein and/or acid salt.

(B) Adapted for feeding of protein and/or fuming liquids.

FIGURE 4 - MODIFIED LABORATORY SLUDGE BLANKET APPARATUS
(SCHEMATIC DIAGRAM)


SEWAGE AND PROTE IN RESERVOIR
SEWAGE, FE+++ COMPOUND, AND ACID RESERVOIR
ADJUSTABLE PINCH CLAMPS
MOTOR
4 LITER BEAKER
INVERTED FUNNEL
AGITATOR
SEWAGE AND PROTEIN RESERVOIR
CACL2 DRYING TUBE
MICROBURET
MOTOR
ADJUSTABLE PINCH CLAMP
CAPILLARY TUBE
RAPID MIXING CHAMBER
PLASTIC BOTTLES (BOTTOMS REMOVED)
MOTOR
4 LITER BEAKER
INVERTED FUNNEL
AGITATOR

(A) FIRST MODIFICATION (CF. FIGURE 3)

(B) SECOND MODIFICATION FOR FEEDING FUMING LIQUIDS

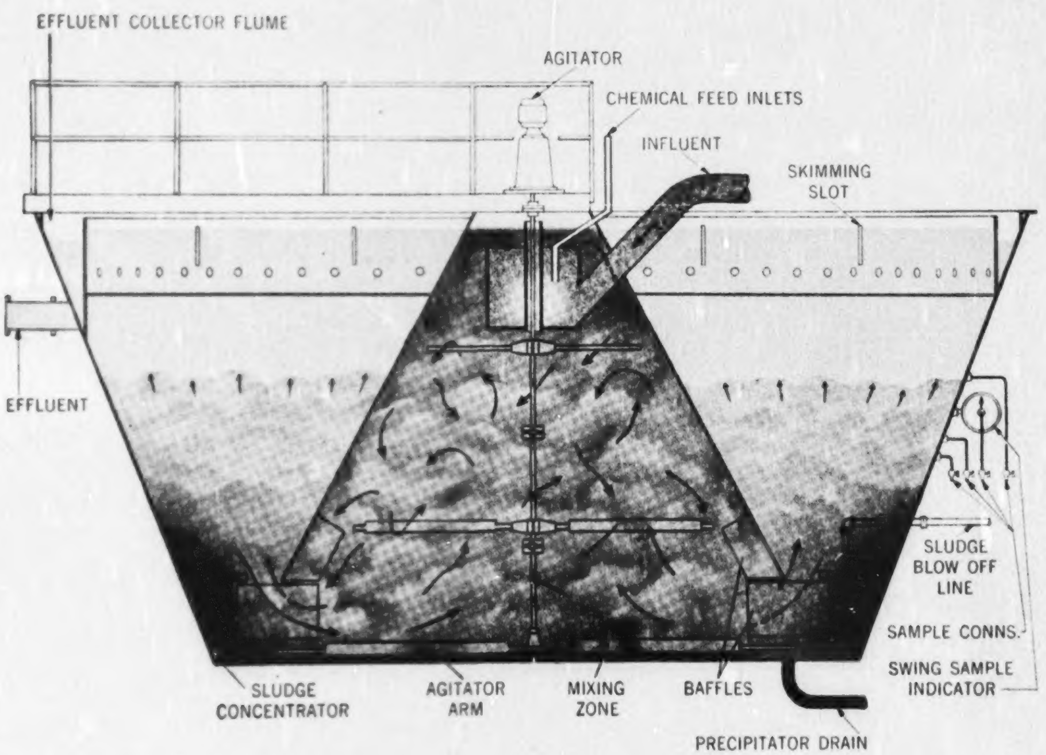

EFFLUENT COLLECTOR FLUME
AGITATOR
CHEMICAL FEED INLETS
INFLUENT
SKIMMING SLOT
EFFLUENT
SLUDGE BLOW OFF LINE
SAMPLE CONNS.
SWING SAMPLE INDICATOR
SLUDGE CONCENTRATOR
AGITATOR ARM
MIXING ZONE
BAFFLES
PRECIPITATOR DRAIN

Figure 5. - PERMUTIT PRECIPITATOR showing thorough mixing of chemicals with influent and previously formed sludge.

-copyright THE PERMUTIT COMPANY, 1955

FIGURE 6
FLOW DIAGRAM
MT. HOLLY, N.J. SEWAGE TREATMENT PLANT
(TRICKLING FILTER PROCESS)

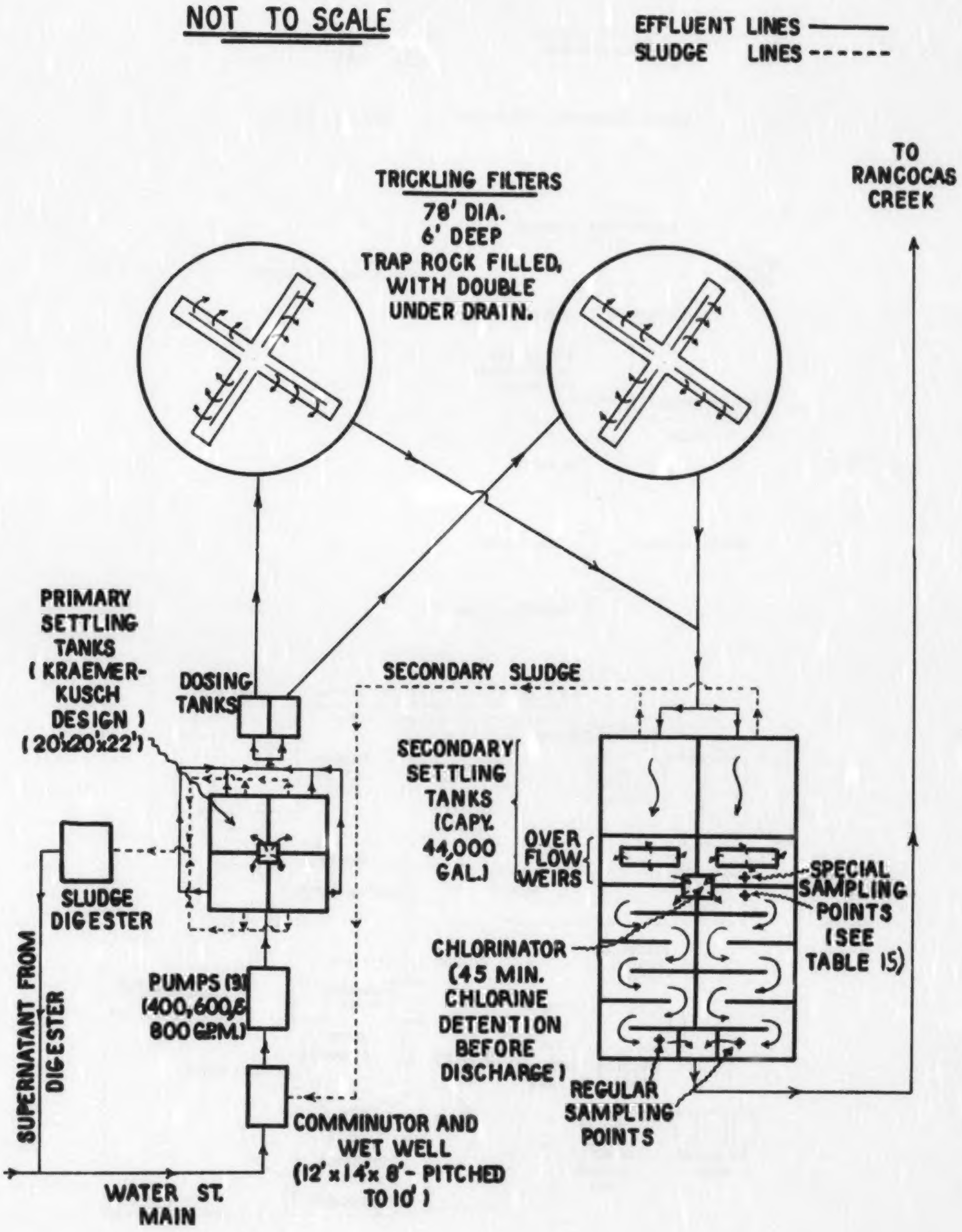
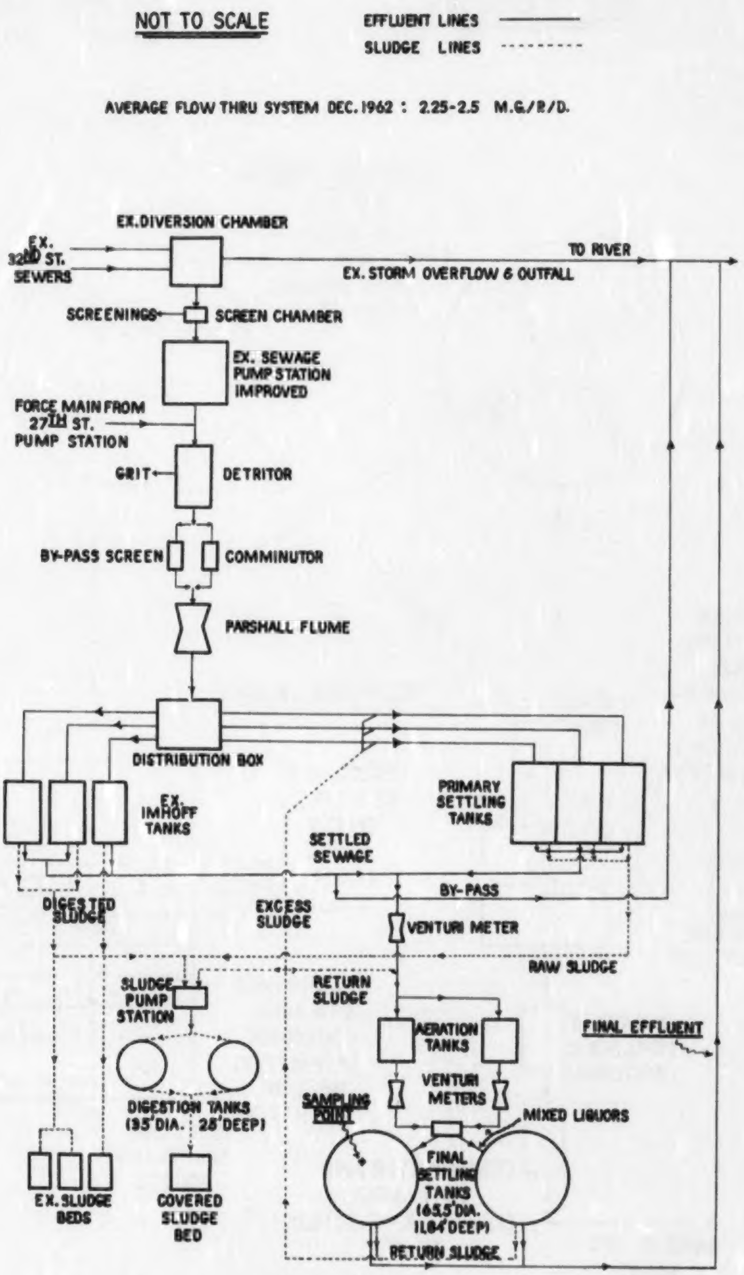

NOT TO SCALE
EFFLUENT LINES ———
SLUDGE LINES - - - - - -
TRICKLING FILTERS
78' DIA.
6' DEEP
TRAP ROCK FILLED, WITH DOUBLE UNDER DRAIN.
TO RANCOCAS CREEK
PRIMARY SETTLING TANKS (KRAEMER-KUSCH DESIGN) (20'x20'x22')
DOSING TANKS
SECONDARY SLUDGE
SECONDARY SETTLING TANKS (CAPY. 44,000 GAL.)
OVER FLOW WEIRS
SPECIAL SAMPLING POINTS (SEE TABLE 15)
SLUDGE DIGESTER
CHLORINATOR (45 MIN. CHLORINE DETENTION BEFORE DISCHARGE)
PUMPS (3) (400,600,& 800 GPM.)
SUPERNATANT FROM DIGESTER
REGULAR SAMPLING POINTS
COMMINUTOR AND WET WELL (12'x14'x 8'- PITCHED TO 10')
WATER ST. MAIN

FIGURE 7
FLOW DIAGRAM
32ND ST. & FARRAGUT AVE. (BALDWINS RUN) SEWAGE TREATMENT PLANT
-ACTIVATED SLUDGE PROCESS-

CAMDEN, N. J.



NOT TO SCALE
EFFLUENT LINES
SLUDGE LINES
AVERAGE FLOW THRU SYSTEM DEC. 1962 : 2.25-2.5 M.G./P/D.
EX. DIVERSION CHAMBER
EX. 32ND ST. SEWERS
TO RIVER
EX. STORM OVERFLOW & OUTFALL
SCREENINGS
SCREEN CHAMBER
EX. SEWAGE PUMP STATION IMPROVED
FORCE MAIN FROM 27TH ST. PUMP STATION
GRIT
DETRITOR
BY-PASS SCREEN
COMMINUTOR
PARSHALL FLUME
DISTRIBUTION BOX
EX. IMHOFF TANKS
PRIMARY SETTLING TANKS
SETTLED SEWAGE
BY-PASS
DIGESTED SLUDGE
EXCESS SLUDGE
VENTURI METER
RAW SLUDGE
SLUDGE PUMP STATION
RETURN SLUDGE
AERATION TANKS
FINAL EFFLUENT
DIGESTION TANKS (35'DIA. 28'DEEP)
VENTURI METERS
SAMPLING POINT
MIXED LIQUORS
FINAL SETTLING TANKS (65.5'DIA. 11.84'DEEP)
EX. SLUDGE BEDS
COVERED SLUDGE BED
RETURN SLUDGE

APPENDIX B

Results

Figures 8-11

Tables 14-19

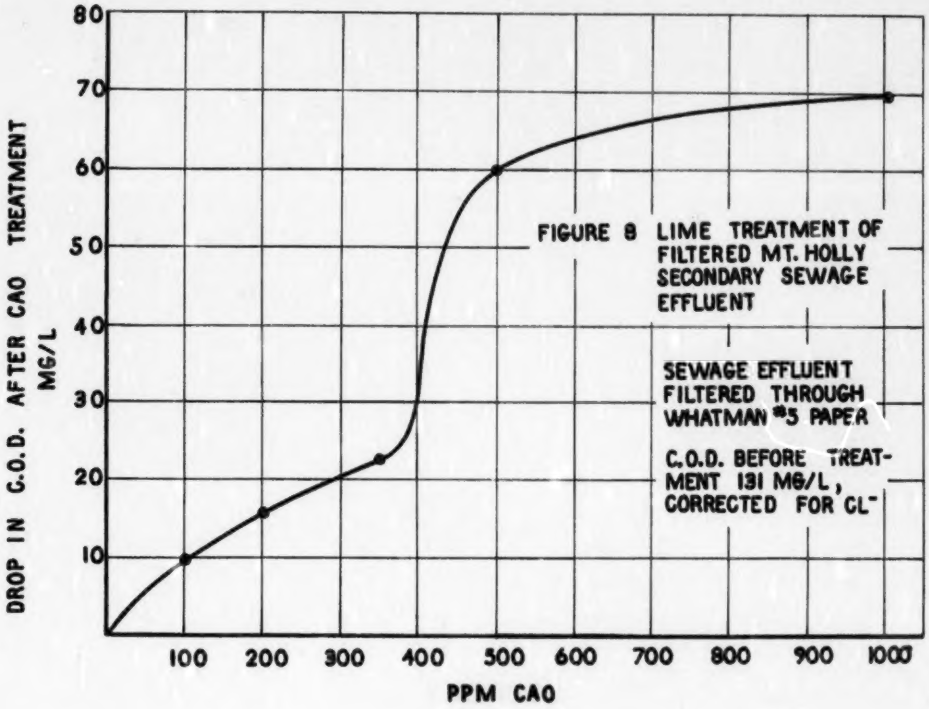


FIGURE 8 LIME TREATMENT OF FILTERED MT. HOLLY SECONDARY SEWAGE EFFLUENT

SEWAGE EFFLUENT FILTERED THROUGH WHATMAN #5 PAPER

C.O.D. BEFORE TREATMENT 131 MG/L, CORRECTED FOR CL⁻

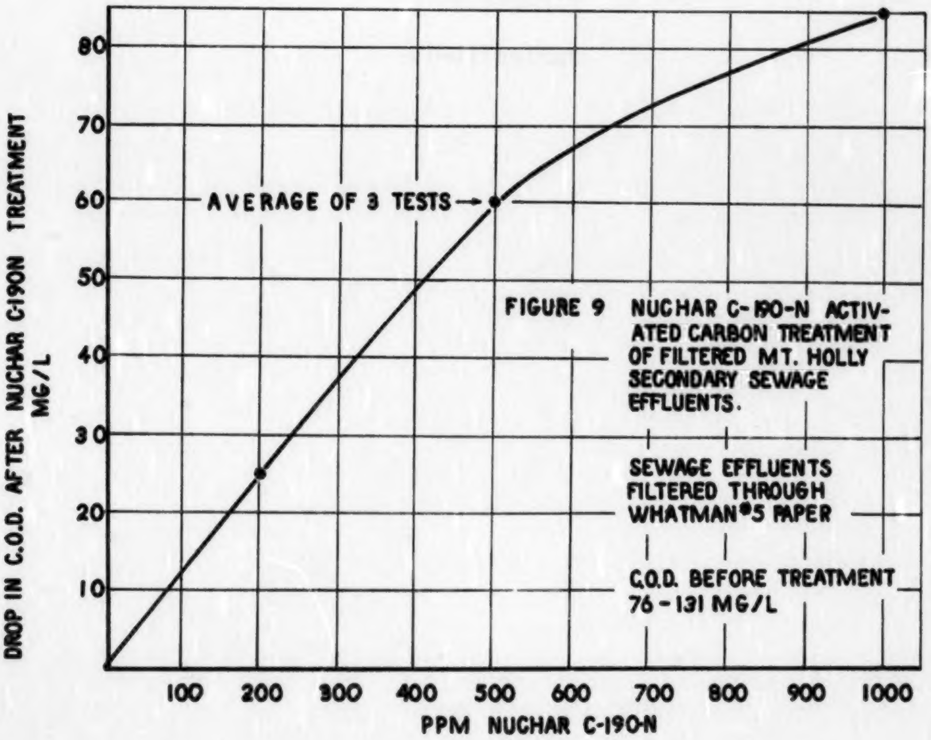


FIGURE 9 NUCHAR C-190-N ACTIVATED CARBON TREATMENT OF FILTERED MT. HOLLY SECONDARY SEWAGE EFFLUENTS.

SEWAGE EFFLUENTS FILTERED THROUGH WHATMAN #5 PAPER

C.O.D. BEFORE TREATMENT 76 - 131 MG/L

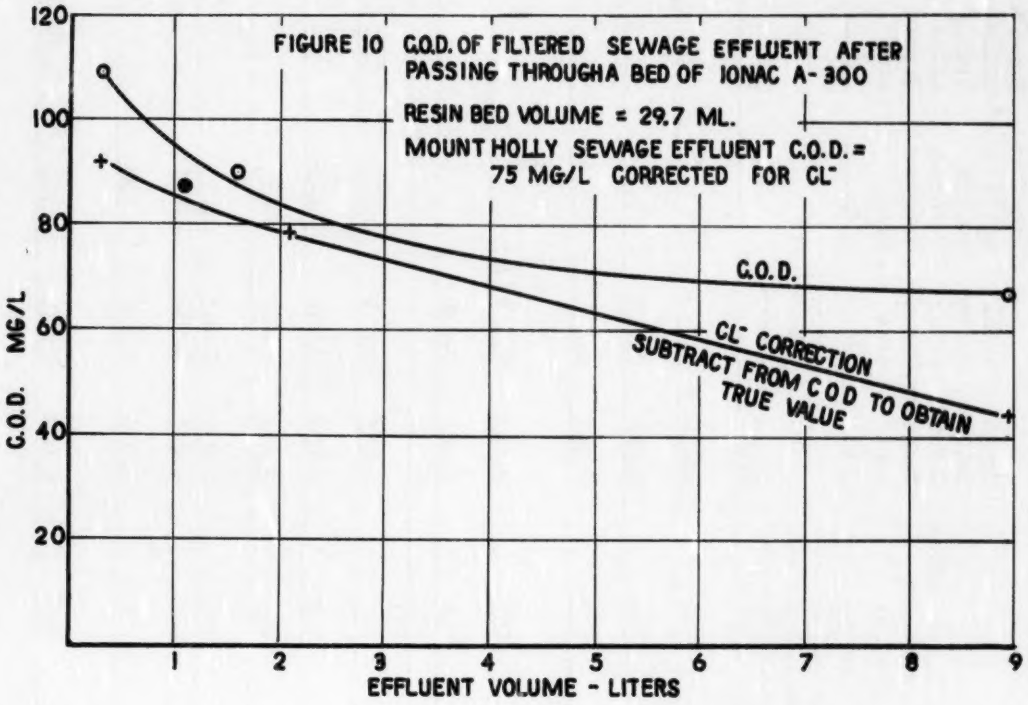


FIGURE 10 C.O.D. OF FILTERED SEWAGE EFFLUENT AFTER PASSING THROUGHA BED OF IONAC A-300

RESIN BED VOLUME = 29.7 ML.

MOUNT HOLLY SEWAGE EFFLUENT C.O.D. = 75 MG/L CORRECTED FOR CL⁻

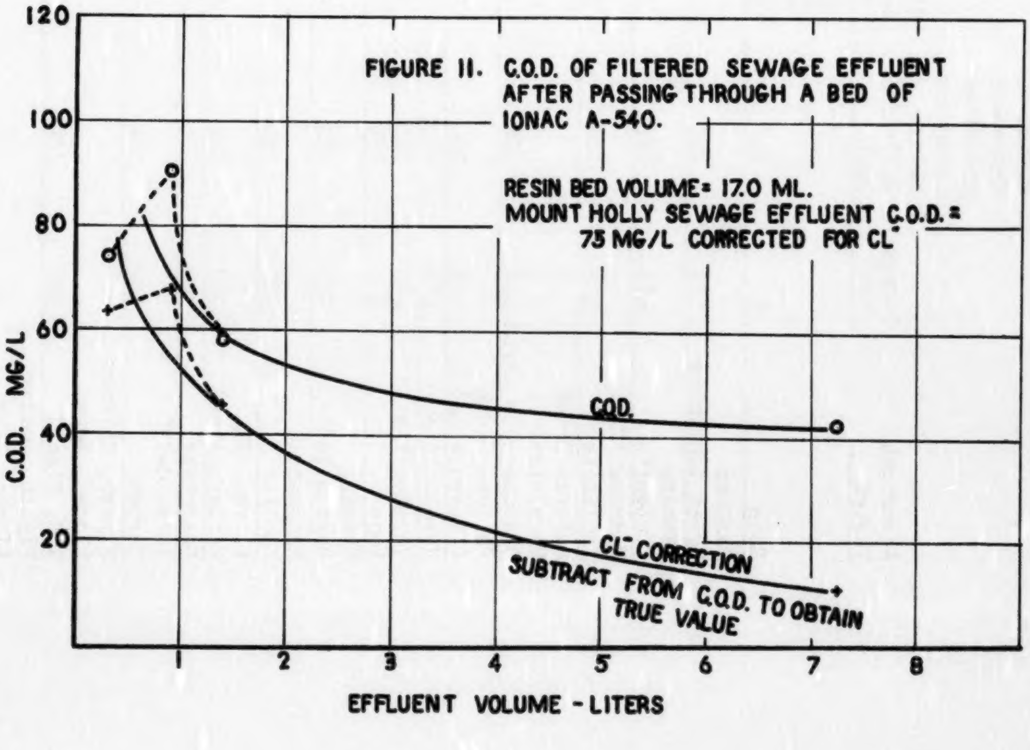


FIGURE 11. C.O.D. OF FILTERED SEWAGE EFFLUENT AFTER PASSING THROUGH A BED OF IONAC A-540.

RESIN BED VOLUME = 17.0 ML.

MOUNT HOLLY SEWAGE EFFLUENT C.O.D. = 75 MG/L CORRECTED FOR CL⁻

Table 14
Adsorbent Testing with Unfiltered Mt. Holly Sewage Effluent

Adsorbent Tested	Dosage PPM	C.O.D. of Untreated Unsettled Secondary Sewage Effluent Mg/L.	Settling Period Minutes	C.O.D. after Settling Period Mg/L.	Total Solids Before Treatment %	Total Solids After Treatment %	Non-Volatile Solids Before Treatment %	Non-Volatile Solids After Treatment %
			0	206				
			20	186		0.036		
			30	157				
None	0	206	90	151	0.042			
Panther Creek Bentonite	416	206	20	122	0.042			
Wyoming Bentonite	416	206	20	139	0.042	0.045		
Hydrite "MP" Kaolinite	416	206	20	127	0.042	0.036		
Natural Dried Uncalcined Diatomaceous Earth	416	206	20	149	0.042	0.039		
Fullers Earth (Attapulgite)	416	206	20	143	0.042	0.036		
Vermiculite	416	203	30	139				
Vermiculite	416	203	90	132				
None	0	184	90	131	0.038	0.035	0.025	0.025
Wyoming Bentonite	382	184	90	118	0.038	0.052	0.025	
Manganese Zeolite	382	184	90	122	0.038	0.036	0.025	
Florex XXX (Attapulgite)	382	184	90	112	0.038	0.033	0.025	
Desertalc	382	184	90	120	0.038	0.038	0.025	
Ionac C-150 Carbon	382	184	90	129	0.038	0.034	0.025	
Flyash, Chimney (Ionac, Bghm. N.J. Plant)	382	184	90	125	0.038	0.034	0.025	0.022
Flyash, Boiler (Ionac, Bghm. N.J. Plant)	382	184	90	125	0.038	0.035	0.025	0.022
Ilmenite	382	184	90	127	0.038	0.033	0.025	

Table 15

A Comparison of Chlorinated and Unchlorinated Mt. Holly Secondary Sewage Effluent

	Unchlorinated	Chlorinated
C.O.D. of unfiltered effluent	208 mg/l.	223 mg/l.
C.O.D. of effluent filtered through Whatman #5 paper	82.4 mg/l.	84.4 mg/l.
Cl^- correction to above C.O.D. values	10.0 mg/l.	12.9 mg/l.
Net C.O.D. of filtered effluents	72.4 mg/l.	71.5 mg/l.
PPM Cl^- of filtered effluent	43.3	56.1
C.O.D. of filtered effluent (Whatman #5 paper) treated with 500 ppm NUCHAR C-190-N	28.7 mg/l.	30.6 mg/l.
Cl^- correction to C.O.D. of carbon treated effluents	11.1 mg/l.	12.2 mg/l.
Net C.O.D. of carbon treated effluents	17.6 mg/l.	18.4 mg/l.
PPM Cl^- of filtered carbon treated effluent	48.1	52.9

Table 16

Adsorbent Testing with Secondary Sewage Effluent, Pre-Filtered Through Whatman #5 Paper

A. Materials Tested as Received

		Dosage, PPM	C.O.D. of Effluent Before Test, Mg/L.*	C.O.D. of Effluent After Test, Mg/L.*	C.O.D. Lowering Effect, Mg/L.	Remarks
Aluminates	Calcium Aluminate	1,000	66	65	1	
Carbonates	Limestone	20,000	42	42	0	
Carbons & Coals	Animal Charcoal (Bone Black)	1,000	66	51	15	
	Nuchar C-190-N	1,000	128	43	85	
		650	81	20	61	
		500	103	44	59	
		500	103	42	61	
		500	77	34	43	
		500	69	10	59	
		500	63	0	63	(Camden Effluent)
		500	75	7	68	(Camden Effluent)
		500	56	0	56	(Camden Effluent)
		400	143	68	75	
		375	47	7	40	(Camden Effluent)
		300	47	6	41	(Camden Effluent)
		250	56	7	49	(Camden Effluent)
		200	128	103	25	
Ion Exchange Resins	Ionac A-540 (Cl-form)	500	51	3	48	(Camden Effluent)
	Ionac A-300 (SO_4-form)	300	47	31	16	(Camden Effluent)
Industrial Wastes, By-Products	Flyash-Cincinnati Gas & Electric	20,000	44	40	4	
	Cement(Stack)Dust-South-Western Portland Cement Co.	20,000	44	36	8	

Table 16 —continued—

		Dosage, PPM	C.O.D. of Effluent Before Test, Mg/L.*	C.O.D. of Effluent After Test, Mg/L.*	C.O.D. Lowering Effect, Mg/L.	Remarks
Metal Oxides	Rutile, Milled	4,000	66	64	2	
	Rutile, Ceramic	4,000	66	62	4	
	Bauxite, Calcined	1,386	122	125.5	0	
	Bauxite, Uncalcined	1,386	122	125.5	0	
	Zirconium Oxide, Dried	650	93	91	2	
Phosphates	Monazite	1,386	125	121	4	
Silicas	Diatomaceous Earth	650	81	79	2	
	Dicalite 426 (perlite)	5,000	85	81	4	
	Dicalite 4106 (perlite)	5,000	85	81	4	
	Dicalite 4156 (perlite)	5,000	85	83	2	
	Celite 545 Mix A	5,000	78	70	8	
	Celite 545 Mix B	5,000	78	68	10	
	Celite 545 Mix C	5,000	78	70	8	
	Celite 545 Mix D	5,000	78	68	10	
	Florisil	20,000	44	40	4	
Silicates	Florex XXX	1,386	125	100	25	
	Attacote	2,000	62	40	22	(Camden Effluent)
	Attacote	1,386	110	96	16	
	Attacote	500	74	57	17	(Camden Effluent)
	Attacote	250	55	52	3	(Camden Effluent)
	Attasorb LVM	10,000	46	60	—	
	Attasorb RVM	5,000	53	62	—	(Camden Effluent)
	Attaclay	500	58	52	6	
	Attagel 20	5,000	53	62	—	(Camden Effluent)
	X-250 (Min. + Chem. Phillip Co.)	5,000	53	62	—	(Camden Effluent)

Table 16 -continued-

		Dosage, PPM	C.O.D. of Effluent Before Test, Mg/L.*	C.O.D. of Effluent After Test, Mg/L.*	C.O.D. Lowering Effect, Mg/L.	Remarks
	Greensand	2,000	95	90	5	
	Greensand	500	63	54	9	(Camden Effluent)
	Greensand	250	95	95	0	
	Edgar ASP 900	10,000	44	51	—	
	Edgar ASP 101	20,000	69	51	18	
	Edgar ASP 403	500	58	58	0	
	Edgar ASP 602	500	58	55	3	
	Vermiculite	692	132	124	8	
	Mica-Waterground	10,000	42	42	0	
	Panther Creek Bentonite	400	128	120	8	
	Molecular Sieve Powder, Type 13X	2,000	53	51	2	(Camden Effluent)
	Yellow Gel	4,000	51	46	5	(Camden Effluent)
	Decalso	2,000	51	53	-	(Camden Effluent)
Sulfates	"Rare Earth Sodium Sulfate" (a sulfuric acid extractive of monazite ore, containing cerium)	2,000	115	117	-	

Table 16 -continued-

B. Laboratory Prepared or Modified Materials

	Dosage, PPM	C.O.D. of Effluent Before Test, Mg/L.*	C.O.D. of Effluent After Test, Mg/L.*	C.O.D. Lowering Effect, Mg/L.	Remarks
Wyoming Bentonite, $ZnCl_2$ treated	1,000	98	91	7	
Greensand, $ZnCl_2$ treated	500	98	94	4	
Bauxite, uncalcined, $ZnCl_2$ treated	500	96	92	4	
Vermiculite, $ZnCl_2$ treated	500	89	89	0	
Attacote, $ZnCl_2$ treated	500	89	75	14	
Wyoming Bentonite, $Zr(SO_4)_2$-H_2SO_4 treated	5,000	84	52	32	
Uncalcined Pikes-Peak Clay-$Zr(SO_4)_2$-H_2SO_4 treated	5,000	84	63	21	
Hydrous Zirconia	3,075 as ZrO_2	44	16	28	
Hydrous Zirconia	692 as ZrO_2	63	50	13	(Camden Effluent)
Isodecyl Diethylene Triamine-imparted onto-Diatomaceous Earth	4,000	81	159	—	

* Corrected for Chlorides.

Table 17
Coagulants and Coagulant Aids in Batch Testing

	Dosage PPM	C.O.D. of Effluent Before Test Mg/L.*	C.O.D. of Effluent After Test Mg/L.*	C.O.D. Lowering Effect Mg/L.	Remarks
Reten	10	76	67	11	
Separan 2610-A	4	194**	208**		
$FeCl_3$	15	66	43	23	
$FeCl_3$	30	66	39	27	
$FeCl_3$	60	97	65	32	pH of $FeCl_3$ tests adjusted to 3.0.
$FeCl_3$	90	66	37	29	
$FeCl_3$	60	97	65	32	
$FeCl_3$	150	102	50	52	
Ferric Sulfate	30	129	88	41	
Ferric Sulfate	60	134	89	45	pH of $Fe_2(SO_4)_3$ tests adjusted to 3.0.
Ferric Sulfate	90	137	66	71	
Alum	30	66	57	9	pH of alum tests adjusted to 6.0.
Alum	60	102	100	2	
Alum	60	66	56	10	
Alum	90	66	55	11	
Titanium Tetrachloride	140	102	73	29	pH 5.75 after addition of $TiCl_4$. No adjustment made.

* Corrected for Chlorides.

**Secondary sewage was as received with no fine paper filtration. Values shown are results after a 90 minute settling period followed by filtration through E + D 615 paper.

Table 18

Batch Coagulation Testing of Proteins and Protein Products

Part A. Gluten Feed Supplement and Casein

Treatment #	C.O.D. of Untreated Filtered Effluent-Corrected For Chlorides, Mg/1.	Treated With	Dosage,* PPM	C.O.D. After Treatment Corrected for Chlorides, Mg/1.	Drop in C.O.D. Due to Treatment Mg/1.	Remarks
1	0 (Tap Water)			0		C.O.D. run on tap water as a blank.
2	0 (Tap Water)	Mix. #1 $FeCl_3$	100 60	15		Protein mixture added to sewage effluent, stirred briefly, then ferric compound added. No pH adjustment made.
3	101	Mix. #1 $FeCl_3$	100 60	115		Same procedure as in Treatment #2.
4	101	Mix. #1 $FeCl_3$	100 60	81	20	Same procedure as Treatment #2, but pH adjusted to 3.2 with 5% H_2SO_4 following addition of the ferric compound.
5	97	$FeCl_3$	60	64.5	32.5	Ferric compound added, stirred briefly, then pH adjusted to 3.3.
6	97	Mix. #2 $FeCl_3$	100 60	99		Same procedure as Treatment #4.

Table 18, Part A -continued-

Treatment #	C.O.D. of Untreated Filtered Effluent-Corrected For Chlorides, Mg/1.	Treated With	Dosage,* PPM	C.O.D. After Treatment Corrected for Chlorides, Mg/1.	Drop in C.O.D. Due to Treatment Mg/1.	Remarks
7	0 (Tap Water)	Mix. #2 $FeCl_3$	100 60	16		Same procedure as Treatment #4.
8	96	Mix. #3 $FeCl_3$	500 225	71	25	Same procedure as Treatment #2.
9	96	Mix. #3 $FeCl_3$	100 60	55	41	Same procedure as Treatment #2.
10	102	Mix. #3	100	77	25	Protein added, stirred briefly, pH adjusted to 3.2 with 1:1 HCl.
11	102	Mix. #3	50	80	22	Same procedure as Treatment #10, but post filtered (Whatman #42) due to fineness of floc.
12	102	Mix. #3 $FeCl_3$	50 30	46	56	Protein added, stirred briefly, pH adjusted to pH 3.2 with 1:1 HCl. Agitated at 50 rpm for 30 minutes. Ferric compound added, and agitation continued for 20 minutes more.
13	102	Mix. #3 $FeCl_3$	25 15	82	20	Same procedure as Treatment #4.

Table 18, Part A -continued-

Treatment #	C.O.D. of Untreated Filtered Effluent-Corrected For Chlorides, Mg/1.	Treated With	Dosage,* PPM	C.O.D. After Treatment Corrected for Chlorides, Mg/1.	Drop in C.O.D. Due to Treatment Mg/1.	Remarks
14	129	Mix. #3 $Fe_2(SO_4)_3$	50 30	91	38	Same procedure as Treatment #12.
15	129	$Fe_2(SO_4)_3$	30	88	41	pH adjusted to 3.1 with 5% H_2SO_4, stirred briefly, then $Fe_2(SO_4)_3$ added.
16	134	Mix. #3 $Fe_2(SO_4)_3$	50 30	89.5	44.5	Same procedure as Treatment #12, but pH adjustment made with 5% H_2SO_4.
17	134	Mix. #3 $Fe_2(SO_4)_3$	50 30	99	35	Same procedure as Treatment #4.
18	134	Mix. #3 $Fe_2(SO_4)_3$	50 60	84	50	Same procedure as Treatment #4.
19	134	$Fe_2(SO_4)_3$	60	89	45	Same procedure as Treatment #5.
20	137	Mix. #3 $FeCl_3$	50 30	87	50	Same procedure as Treatment #12, but pH adjustment made with 5% H_2SO_4.
21	137	Mix. #3 $Fe_2(SO_4)_3$	50 30	105	32	Protein added, agitated for 20 minutes at 50 rpm, then ferric compound added and agitation continued for 20 minutes more, then pH adjusted to 3.1 with 5% H_2SO_4 and agitation continued for 10 minutes more.

Table 18, Part A -continued-

Treatment #	C.O.D. of Untreated Filtered Effluent-Corrected For Chlorides, Mg/1.	Treated With	Dosage,* PPM	C.O.D. After Treatment Corrected for Chlorides, Mg/1.	Drop in C.O.D. Due to Treatment Mg/1.	Remarks
22	137	Mix. #3 $Fe_2(SO_4)_3$	50 60	90	47	Same procedure as Treatment #21.
23	137	$Fe_2(SO_4)_3$	90	66	71	Same procedure as Treatment #15.
24	137	Mix. #3 $FeCl_3$	50 30	74	63	Conditions similar to Treatment #12, but time intervals not strictly adhered to, and pH adjustment made with 1:1 HCl.

* Dosage values for Mixtures #1 and #2 were in ppm of the total mixture.

Dosage values for Mixture #3 were in ppm of casein.

Dosage values for $Fe_2(SO_4)_3$ were in ppm of $Fe_2(SO_4)_3$ calculated as ppm of $FeCl_3$.

Consult text for material composition.

Table 18 (Cont'd)

Part B. Zein, Casein, and Soya Treatments

Treatment #	C.O.D. of Untreated Filtered Effluent Corrected For Chlorides Mg/1.	Treated With	Dosage,* PPM	C.O.D. After Treatment Corrected For Chlorides Mg/1.	Drop in C.O.D. Due to Treatment Mg/1.	Remarks
1	61	Mix. #4 $FeCl_3$	50 60	39	22	Protein dispersion added to sewage effluent, stirred briefly, then pH adjusted to 3.1 with 1:1 HCl. Agitated 30 minutes. $FeCl_3$ added. Agitated 20 minutes more.
2	59	Mix. #4 $FeCl_3$	50 60	35	24	Same procedure as in Treatment #1.
3	61	Mix. #4 $FeCl_3$	100 60	49	12	Same procedure as in Treatment #1.
4	59	Mix. #4 $FeCl_3$	100 80	43	16	Same procedure as in Treatment #1.
5	59	Mix. #5 $FeCl_3$	50 60	55	4	Same procedure as in Treatment #1.
6	59	Mix. #5 $FeCl_3$	100 80	103	(+44)	Same procedure as in Treatment #1.
7	0 (tap water)	Mix. #4 $FeCl_3$	50 60	4	(+4)	Same procedure as in Treatment #1, but final pH adjustment made (to 6.2) with Na_2CO_3.
8	0 (tap water)	Mix. #4 $FeCl_3$	100 80	11	(+11)	Same procedure as in Treatment #7.

Table 18, Part B -continued-

Treatment #	C.O.D. of Untreated Filtered Effluent Corrected For Chlorides Mg/l.	Treated With	Dosage,* PPM	C.O.D. After Treatment Corrected For Chlorides Mg/l.	Drop in C.O.D. Due to Treatment Mg/l.	Remarks
9	0 (tap water)	Mix. #5 $FeCl_3$	50 60	14	(+14)	Same procedure as in Treatment #7.
10	0 (tap water)	Mix. #5 $FeCl_3$	100 80	3	(+3)	Same procedure as in Treatment #7.
11	64	Mix. #4 $FeCl_3$	50 60	45	19	Protein added to sewage effluent, mixture agitated 5 minutes, then pH adjusted to 3.1 with 1:1 HCl. Mixture agitated 15 minutes more, then $FeCl_3$ added. Mixture agitated an additional 15 minutes, then pH adjusted to 6.2 with $Ca(OH)_2$.
12	64	Mix. #4 $FeCl_3$	100 80	34	30	Same procedure as in Treatment #11.
13	64	Mix. #5 $FeCl_3$	50	44	20	Same procedure as in Treatment #11.
14	64	Mix. #5 $FeCl_3$	100 80	39	25	Same procedure as in Treatment #11.
15	101	Mix. #6 $FeCl_3$	50 30	61	40	Protein added to sewage, pH adjusted to 3.3 with HCl. Agitated 30 minutes. Added $FeCl_3$ and agitated 20 minutes more.

* Protein dosages based on weight of protein in dispersion.

Table 18 (Cont'd)

Part C. Food-Grade Gluten Treatments

Treatment #	C.O.D. of Untreated Filtered Effluent Corrected for Chlorides Mg/1.	Treated With	Dosage,* PPM	C.O.D. After Treatment Corrected for Chlorides Mg/1.	Drop in C.O.D. Due to Treatment Mg/1.	Remarks
1	99	Mix. #7 $FeCl_3$	75 45	56	43	pH adjusted with HCl to 2.9-3.1 range after adding gluten and $FeCl_3$. pH adjusted to 6.0-6.2 with CaO after coagulation and contact time.
2	99	Mix. #7 $FeCl_3$	100 60	61	38	Same as Treatment #1
3	99	Mix. #7 $FeCl_3$	150 90	57	42	Same as Treatment #1
4	99	Mix. #7 $FeCl_3$	200 120	56	43	Same as Treatment #1
5	98	Mix. #7 $FeCl_3$	75 45	64	34	No neutralization after coagulation.
6	98	Mix. #7 $FeCl_3$	200 120	51	47	Same as Treatment #5
7	98	Mix. #7 $FeCl_3$	75 45	52	46	Same as Treatment #1, but post-adjustment to pH 6.5.
8	98	Mix. #7 $FeCl_3$	200 120	51	47	Same as Treatment #7

* Gluten dosages based on weight of Gluten in dispersion.

Table 19

Batch Treatments Employing Mixtures of Adsorbents, Coagulants and Oxidants. Sewage not Prefiltered.

Treatment	C.O.D. of Untreated, Unfiltered, Secondary Sewage Effluent, Mg/L.	C.O.D. after Treatment, Mg/L.
208 ppm Panther Creek Bentonite & 112 ppm of $TiCl_4$	176	66
60 ppm $FeCl_3$, then 0.8 ppm $Ca(OH)_2$. Filtered through E + D 615 paper following agitation, then again treated with 200 ppm Nuchar C-115.	161	75
20 ppm $KMnO_4$ 60 ppm $FeCl_3$ 0.8 ppm $Ca(OH)_2$. Mixture agitated, then filtered through E + D 615 paper. Post-treated with 200 ppm Nuchar C-115.	149	52
20 ppm $KMnO_4$. Agitated, filtered, then post-treated with 400 ppm Nuchar C-115.	149	56
450 ppm milled rutile in 8060 ppm H_2SO_4 - plus 4600 ppm CaO (to precipitate acid dissolved titanium) plus 6800 ppm Na_2CO_3 to neutralize treated mixture to pH 6.8.	266	124

Table 19 -continued-

Treatment	C.O.D. of Untreated, Unfiltered, Secondary Sewage Effluent, Mg/L.	C.O.D. after Treatment, Mg/L.
45 ppm milled rutile in 810 ppm H_2SO_4 plus 2000 ppm $BaCO_3$ plus 7400 ppm Na_2CO_3 (to achieve alkalinity in mixture) then 60 ppm $FeCl_3$ (Final pH adjusted to 6.8 with additional 110 ppm H_2SO_4.	266	137

APPENDIX C

U.S. Patent 2,393,269

and

"Wastewater Utilization by Clarification"

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Patented Jan. 22, 1946 **2,393,269**

UNITED STATES PATENT OFFICE

2,393,269

COAGULANT COMPOSITION FOR REMOVAL OF SUSPENDED OR DISSOLVED MATERIALS FROM LIQUIDS

Willem Rudolfs, Piscataway Township, Middlesex County, and Harry W. Gehm, Metuchen, N. J., assignors to The Permutit Company, New York, N. Y., a corporation of Delaware

No Drawing. Application October 2, 1941,
Serial No. 413,298

7 Claims. (Cl. 252—181)

This invention relates to the treatment of liquids such as sewage, trade wastes and similar aqueous liquids containing colloidal, suspended or dissolved matter which should be at least partially separated from the liquids. The invention relates more particularly to a new coagulant for treating such liquids, to the method of making the coagulant, and to methods of treating liquids therewith.

Metallic salts such as alum and ferric chloride have been used to coagulate and settle or render filterable the suspended matter in various liquids. In fact, ferric chloride is used extensively with sewage for this purpose, even though it is fairly expensive and objectionable because of its corrosiveness and for other reasons.

We have found that coagulating salts of the multivalent metals such as the chlorides of iron, aluminum, zinc, tin, titanium, chromium, manganese and copper when used in conjunction with various proteinous materials such as gelatine, glue or the like, are very effective coagulants. Such a combination produces equivalent clarification at lower cost compared with ferric chloride alone, or better results may be obtained at equal cost.

Although separate solutions of the metallic salt and proteinous material may be fed to the liquid to be treated, we have found that these ingredients may be used advantageously in a combined form. In general we have found that similar compound formation does not take place with other metal salts, e. g., sulfates or carbonates. Furthermore in such cases the mixtures of the metal salts with the protein materials still show some advantage over the use of the metal salts alone, but this advantage is not as great as that obtained by the use of the protein material metal chloride compounds.

For example, ferric chloride and gelatine may be combined to give a composition of matter in which the gelatine and ferric chloride apparently are chemically combined and which is highly effective as a coagulant and is very convenient for storage, transportation and use.

The quantity of ferric chloride required in this combination for the clarification of liquids such as sewage is substantially smaller than the quantity of ferric chloride that would be required when used alone, and a very rapid and effective formation and settling of floc is obtained. Also, a higher degree of clarification can be obtained with such a combination than is obtainable with economically practical dosages of straight ferric chloride.

Various proteinous materials such as glue, zein, gluten, casein and albumen may be substituted for the gelatine but we have found gelatine of commercial grade (not refined for use as food) to be most satisfactory from the standpoint of cost and efficiency. Some of the other proteinous materials, which generally must be used in their impure forms on account of cost, tend to clarify liquids imperfectly and/or contain inactive ingredients which dissolve in the liquid and contribute to its impurity. Glue, for instance, apparently contains protein degradation products which dissolve in the liquid, and is generally less efficient as a purifying agent in combination with the ferric chloride than is gelatine although it is generally second best of the available proteinous materials. It will be appreciated that such proteinous materials as are capable of use in combination with ferric chloride, in their impure or crude forms which are available for use in treating sewage and industrial wastes, vary widely in composition and such considerations may determine the particular proteinous material to be used in the clarification of a particular liquid at a particular time and place. Such other proteinous materials apparently owe their utility to their content of protein which is identical with or similar to that of gelatine.

Due to the wide variations in proteinous materials, including gelatine, available for use, and to the wide variations in the character of liquids requiring clarification, it is impossible to state a concise rule as to the best ratio of metallic salt to proteinous material and the best quantity of the composition to use for treating all liquids. The following disclosure is to be read and understood in the light of this situation. Those skilled in the arts of liquid clarification and sewage treatment appreciate the extreme variations encountered in practice and demand a highly flexible means for meeting special conditions. The following disclosure will not therefore be regarded by those skilled in the art as being lacking in specific and critical data.

Coagulants comprising a metallic salt such as ferric chloride in combination with a proteinous material may be prepared in various ways. For example, a suitable compound may be prepared by grinding together about 1 to 7 parts of dry gelatine and 5 parts of anhydrous ferric chloride with just sufficient water so that the compound can be kneaded to a uniform paste. The paste can be stored as such, evaporated to produce a dry product, or diluted with water to form a stable liquid product. A dilution such that one gallon of solution contains 0.25 lb. of iron is satisfactory.

A suitable compound or composition may also be prepared by simply mixing gelatine and ferric chloride in the presence of water. Solutions of ferric chloride and gelatine may be simply mixed to produce a solution of the composition ready for use. The concentrations of the solutions are not critical but we prefer substantially saturated solutions. Dilute solutions are inconvenient for storage and shipment, and highly dilute solutions are not stable in storage.

Compositions prepared by simply mixing solutions of the gelatine and ferric chloride may be concentrated by evaporation and even reduced to dryness but for the production of a dry composition we prefer to grind the gelatine and anhydrous ferric chloride together in the presence of only sufficient water to moisten the mixture. The product may be dried in the air or by the application of heat and powdered or flaked for convenience in handling and ready solubility. When the gelatine and ferric chloride are ground together heat is evolved and a solution of the product in water exhibits freezing points and vapor pressure changes, pH characteristics, speed of solubility, and other characteristics, all of which indicate that the ferric chloride and gelatine have entered into chemical combination. In fact, the ferric chloride is less corrosive in this combination and cannot be separated by washing out of the product with cold water as it could be if it were simply mixed and not combined with the proteinous material.

As stated above, the proportions in which the proteinous material and metallic salt may be combined vary within a wide range. Gelatine has been found to be effective when combined with ferric chloride in proportions as low as 1 part by weight of dry gelatine to 5 parts by weight of anhydrous ferric chloride and possibly even a smaller proportion of gelatine may be effective under some circumstances. Ordinarily, however, the ratio of gelatine to ferric chloride should not be less than 1 to 3 and the customary range is 1 part of gelatine to from 1 to 2 parts of ferric chloride. On the other hand, it is not considered practical or economical to combine more than about 4 parts of gelatine with 3 parts of ferric chloride. The best proportions for gelatine and ferric chloride appear to be 2 parts gelatine to 3 parts ferric chloride. This combination is definitely superior with respect to stability, lack of corrosiveness, solubility in water, and ability to dry well and remain as a dry product without taking up water.

In general, the proteinous material, when combined with ferric chloride, should be combined in the proportion of about 1 to 7 parts of the former for each 5 parts of the latter, by weight. With other metallic salts than ferric chloride, the proportion of proteinous material to be added is increased or decreased so that the time required for the appearance of the first visible floc is approximately the same as that obtained with the foregoing proportions of proteinous material to ferric chloride.

Under some circumstances when adding the proteinous material-metallic salt combination to liquids, it is found advantageous to dilute a concentrated solution of the compound with ferric chloride or similar salt solution instead of with water. When this is done, we ordinarily use a compound containing a ratio of proteinous material to ferric chloride of 2 to 3, but the ratio in the diluted solution does not fall below 1 to 5. Even at this low ratio, the proteinous material combined with the ferric chloride or similar salt materially aids the flocculation of suspended solids.

Another example of a method of making a good coagulant is as follows. Dissolve gelatine in hot water, say 3 parts by weight of gelatine to 20 parts of water and then add the ferric chloride, say 2 parts. The mixture quickly stiffens and kneading is necessary to complete the reaction. The resulting pasty compound may be stored and shipped as such or dissolved in water or dried, preferably in the form of flakes. The dry product, the paste and even concentrated solutions are quite stable, non-hygroscopic and relatively non-corrosive. This solution if diluted to such a degree that one gallon of the liquor contains ¼ lb. of iron will remain stable indefinitely. If the composition is diluted to such an extent that 1 gallon contains 1/16 lb. of iron, it will remain stable for about two weeks. Higher dilutions will change in color from dark brown to yellow within about 24 hours and such solutions lose, to a large extent, their coagulating properties. Such highly diluted solutions are however stable for a few hours, say up to 10 hours, and the instability of the dilute solutions prepared for immediate use does not introduce a troublesome factor.

The coagulants of our invention may be applied to liquids to be clarified in the usual manner as will be understood by those skilled in the art. The coagulant ingredients may be fed separately or combined in solution form, or the compound may be fed in solid form. Usually, dilute solutions of the coagulant are easier to handle and can be fed in more accurate proportions to the liquid to be clarified. Some agitation of the liquid after addition of the coagulant is usually desirable since the floc settles very rapidly.

The clarification process and coagulants of our invention are particularly effective for the treatment of sewage and industrial wastes, but may also be used for general water coagulation processes. In some cases, however, it may be desirable to feed turbidity, i. e., clay or similar material, along with the coagulant or coagulant ingredients into the liquid to be treated in order to obtain the best results.

The proportion of coagulant required will vary with the liquid to be treated, the degree of treatment required, the composition of the coagulant, and many other factors. For treating average domestic sewage (approximately 200 P. P. M. total suspended solids and 200 P. P. M. B. O. D.) a suitable solution may be fed to provide in the sewage 4 to 8 parts of gelatine and 20 to 60 parts of ferric chloride per million. With more dilute sewages, lower concentrations may be used. In general, the proteinous material-metallic salt compound can be used with good results to provide only about 50 to 80% as much metal as would be required if the metallic salt were used alone.

Ordinarily in sewage treatment, the ferric chloride-gelatine combination works better at pH values below 7 than at pH values above 7. Its effectiveness increases with decreasing pH values within the range from about 8.0 down to pH 2.5. Above pH 8 the floc particles formed are smaller than at lower pH values and at a pH value of 11 the clarification of the sewage is definitely imperfect.

Perhaps the most important characteristic of the action of the metallic salt-proteinous material combination when operating conditions are normal is the character of the floc formed and its speed of formation. When the proteinous material and metallic salt are used jointly, observation indicates that the time required for the appearance of the first visible floc (under specified conditions of lighting, etc.) is substantially increased as compared with the time required for such floc appearance when the metallic salt is used alone. This makes it possible for the coagulating chemicals to be more thoroughly dispersed throughout the liquid before the actual clumping together of the small floc particles into larger floc aggregates takes place. Thus the smaller floc particles have a better opportunity to come in contact with the suspended and dissolved matter to be removed before the actual formation of the floc aggregates takes place. But the total time period for the formation of the first visible floc is extremely small compared with the time required for the entire coagulation process which may be said to include three stages, viz.: (*a*) formation of first visible floc, (*b*) clumping together of small floc particles into larger aggregates, and (*c*) settling of these floc aggregates with the occluded suspended and dissolved matter. However, once the floc has started to form, the clumping together into the larger aggregates proceeds more rapidly than in the case of the straight metallic salt and also the aggregates so formed are larger, more stable and tougher, so that they do not break up on being disturbed and even when broken up by violent stirring or pumping, reform and settle.

Sewage which has been properly treated with the composition has about the same B. O. D. and oxygen consumed values as sewage which has been properly treated with ferric chloride alone. This proves that the added proteinous material is removed with the floc and does not remain in the clarified effluent for, if it remained, these values would be higher.

The sludge formed maintains its flocculated form even after decomposition sets in and resists redispersion. Of the various proteinous materials, gelatine gives the largest reduction in the ferric chloride requirements for complete clarification of a sewage. Some other proteinous materials, however, give a large floc but impurities or non-proteinous materials present tend to dissolve in the sewage effluent and increase the oxygen demand. Others are satisfactory except for the fact that they fail to reduce appreciably the amount of ferric iron required for clarification over that necessary when $FeCl_3$ alone is employed.

Results similar to those obtained by the use of the described proteinous material-metallic salt combination may be obtained by proper use of proteinous material and metallic salt introduced separately into the liquor to be treated. For example, gelatine may be first added and thoroughly distributed and ferric chloride may then be added and quickly and thoroughly distributed. If the metallic salt is added before adding the proteinous material, e. g. about 1 minute earlier, the advantages of the combination are lost, and if the ingredients are added simultaneously, some advantage is obtained but the results are not as good as are obtained by using the proteinous material-metallic salt compound or by adding the proteinous material before the metallic salt. Even when the proteinous material is fed to the liquid before the metallic salt, however, it is necessary to control the ratio of proteinous material to metallic salt and this problem is eliminated by the use of the compound of the two ingredients.

The metallic salt-proteinous material combinations of our invention may be used, like ferric chloride and other coagulants, with additions of lime and other treating agents. Gelatine, whether added separately or in combination with ferric chloride, reduces the ferric chloride requirements but use of the combination definitely avoids the possibility of substantial quantities of the gelatine escaping flocculation and remaining the liquid effluent.

Sludge produced by the combination is more stable, remains amenable to dewatering longer and loses its dewatering characteristics more slowly than a ferric chloride sludge which, if allowed to stand too long, becomes gelatinous and must be treated, e. g., with lime and ferric chloride to restore its dewatering properties. The ferric chloride-gelatine sludge filters well and yields a firm non-gelatinous cake containing less water than a ferric chloride sludge. The proportions stated in the claims are in terms of parts by weight.

The terms and expressions which we have employed are used as terms of description and not of limitation, and we have no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but recognize that various modifications are possible within the scope of the invention claimed.

We claim:

1. A coagulant for use in removing dissolved or suspended matter from liquids comprising ferric chloride and gelatine combined in the proportion of about 1 to 7 parts by weight of gelatine to 5 parts by weight of ferric chloride.

2. A coagulant for use in removing dissolved or suspended matter from liquids comprising about 1 to 2 parts by weight of a chloride of a trivalent metal combined with 1 part by weight of an albuminous protein.

3. A coagulant composition for use in removing dissolved or suspended matter from liquids comprising a compound of 5 parts by weight of a chloride of a trivalent metal chemically combined with about 1 to 7 parts by weight of an albuminous protein, said compound being dissolved in a dilute solution of hydrochloric acid.

4. A coagulant composition for use in removing dissolved or suspended matter from liquids comprising a compound of 5 parts by weight of a chloride of a trivalent metal chemically combined with about 1 to 7 parts by weight of gelatine, said compound being dissolved in a dilute solution of said salt.

5. A method of preparing a coagulant for use in removing dissolved or suspended matter from liquids comprising mixing in the presence of sufficient water to form a thick paste about 1 to 7 parts by weight of an albuminous protein with about 5 parts by weight of a chloride of a trivalent metal.

6. A method of preparing a coagulant for use in removing dissolved or suspended matter from liquids comprising grinding together 1 to 7 parts by weight of solid gelatine and 5 parts by weight of ferric chloride together with just sufficient water to form a pasty mass.

7. A method of making a coagulant for use in removing dissolved or suspended matter from liquids comprising dissolving about 3 parts by weight of gelatine in about 20 parts by weight of water, adding about 2 parts by weight of ferric chloride to the solution, and kneading the resulting pasty mass.

WILLEM RUDOLFS.
HARRY W. GEHM.

Waste Water Utilization by Clarification[*]

By Charles Carpenter[1] and Cover C. Porter[2]

Abstract

Utilization of waste waters by removing suspended pulp fibers in a Spaulding type precipitator was carried through laboratory and pilot plant stages. A 1200 g.p.m. industrial sized unit was then developed which takes feed water containing 2 to 3 pounds per thousand gallons solids and delivers a clarified effluent containing 0.1 pounds per thousand gallons or less. Operation is continuous and trouble free. No extraneous chemicals or flocculating agents are required.

The initial units of Southland Paper Mills, Inc. consisted of the groundwood mill, one 234-inch fourdrinier, power plant, and necessary auxiliaries for the production of approximately 165 tons of newsprint per day. Water was supplied from five deep wells approximately 1000 feet deep in the Carrizo stratum. As a matter of economical operation, emphasis was placed on all possible reuse of white water within the groundwood mill and newsprint mill.

In the latter part of 1941, plans were laid for the addition of a 175 ton kraft mill. In order to economize on water, it was felt that further utilization of waste effluents that go out of the mill should be investigated from a viewpoint of using these waters in a manner not ordinarily done in the pulp and paper industry. In the early months of 1942, a suggestion was made by the Permutit Company that the Spaulding type precipitator might be employed to separate the suspended solids in these waste effluents from the water so that either one or both could be reused back in the system. As the suspended solids content of the waste effluents consisted entirely of wood fiber, the presentation of this idea was radically different from the utilization of the Spaulding type precipitator for other uses. The main use of the Spaulding precipitator had been for the removal of hardness from water in which the principle of operation is the formation of nuclei of precipitated material upon which more of the precipitate could form. The passage of the raw hard water and the treatment chemicals passing through a sludge bed of this precipitated material greatly reduced the time interval and retention period necessary for the removal of hardness from industrial waters. Another use of the Spaulding type precipitator is for removing silt from waters in which the principle involved is the flocculation and loading of the silt with some agent such as alum and passing the raw water through a sludge bed of this flocculated material. The waste effluent from a paper mill, however, contained an entirely different type of suspended material and, as it worked out, the suspended fiber acts as its own flocculating agent and its own loading agent, although, of course, no chemical actions are involved.

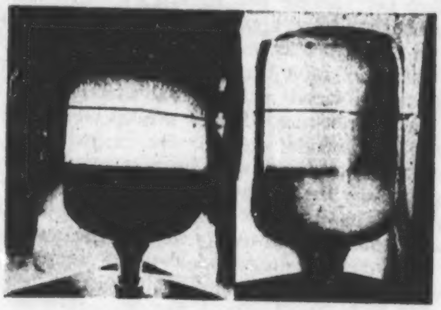

Fig. 2
Sludge Blanket Formed in Operation of Laboratory Apparatus

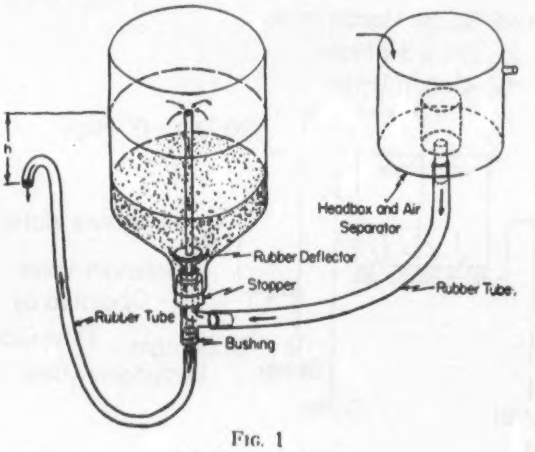

Fig. 1
Laboratory Apparatus

As prior jar tests conducted by the equipment manufacturer had shown that the principle of fiber sludge blanket clarification looked promising, further laboratory experiments were then conducted at the mill on typical waste water effluents.

Laboratory Experiments

In conducting the laboratory experiments to determine if the Spaulding type precipitator principle could separate the suspended fiber from the accompanying water in continuous operation, cylinder tests were first made to study the settling rate of these solids. White water, or waste effluent from the main sewer, was placed in 1000 ml. graduated cylinders and it was observed that the suspended fibers would settle very readily if the total solution was not contaminated with air bubbles. If the solution was contaminated with air it was found that minute bubbles clung to the individual fibers and caused them to float and congregate at the top of the cylinder instead of at the bottom. It was therefore seen that the first step to take in setting up a continuous operation experiment was to remove the air from the water. An apparatus was therefore devised as shown in Fig. 1. Water to be tested was passed into the small headbox which was so arranged that the effluent from the box was drawn off beneath the surface of the water which allowed the air bubbles to rise and escape from the surface. The mixture of water and suspended pulp fibers passed into the bottle until it was full and then overflowed down the ¼-inch pipe to which a rubber hose was fitted for the purpose of varying the rate of flow by raising or lowering the point of discharge. The initial flow was started at a very low rate in order to build up a sludge blanket of settled fiber and then increased to a value which would give a flow rate of approximately 1 gallon per minute per square foot of bottle area. Figure 2 shows the appearance of the sludge blanket as it was in the continuous operation of Fig. 1. This sludge blanket had a gently rolling motion and the incoming water as it passed through the sludge zone left the suspended fiber behind and fairly clear water overflowed down into the ¼-inch pipe. The photograph was also taken by a transmitted light in order to show the clean line of demarkation between the sludge zone and the clarified water above. Figure 3 shows the component parts which consist of a ¼-inch pipe threaded for about 3 inches on the bottom end, a ¼-inch to ½-inch bushing, a ½-inch tee, a ½-inch closed nipple, and a ½-inch by 3-inch nipple. A rubber stopper to fit the 5-gallon bottle and bored to fit the ½-inch by 3-inch nipple plus a rubber deflector made out of gasket material complete the pieces. The influent passed into the ½-inch nipple from the combination air separator and headbox and the effluent overflowed into the top of the ¼-inch pipe inside the bottle and passed out through a rubber tube which was slipped over the small piece of ¼-inch piping seen protruding from the bushing which is screwed into the tee.

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[*] Presented by title at the Annual Meeting of the Technical Association of the Pulp & Paper Industry, Hotel Commodore, New York, N. Y., Feb. 19-22, 1945.

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As there were no means to draw off the concentrated sludge after it had been left behind in the bottle, the maximum duration of the individual runs was only about 3 hours after which time the sludge became so heavy that it boiled up into the clarified water zone and necessitated starting all over again with an empty bottle. Table I is a summary of typical results obtained from the inverted bottle clarification experiments.

It was felt that the results as shown in Table I justified further investigation of the Spaulding precipitator theory of continuous removal of suspended pulp from water. It was decided therefore to carry on this investigation with a pilot plant.

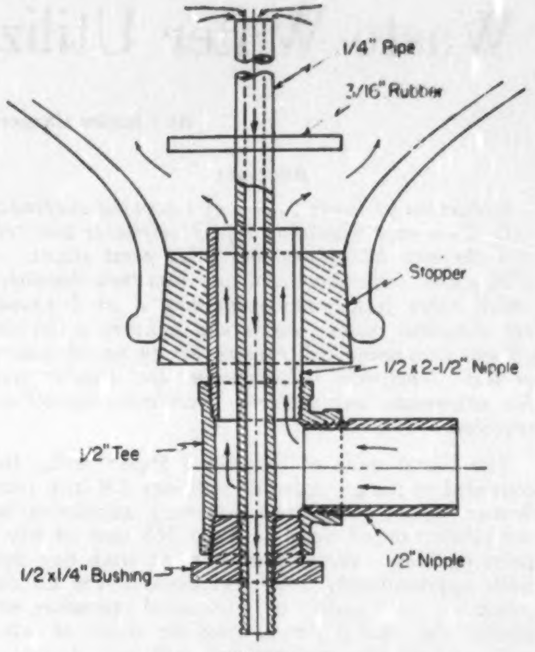

FIG. 3
Detail of Inlet Assembly

The pilot plant work was started in the spring of 1942 and completed in the early summer of the same year. A small precipitator, 3 feet in diameter and 5 feet high, was obtained from the Permutit Company and certain home-made auxiliaries were made at the mill. As shown in Fig. 4, a 50-gallon drum was used as a headbox and also acted as an air separator by placing a 5-gallon can in the bottom and above the takeoff so that air bubbles were allowed to rise to the surface. Internal construction of the precipitator is also shown in a simplified form. Waste effluents supplied from the headbox passed into the conical section, passed under the edges at the bottom of the tank, and rose to a collecting launder from whence it flowed out of the unit by gravity. An external sludge concentrator was made from a 50-gallon drum consisting essentially of an open pan in the bottom of the drum where the sludge could settle and be periodically withdrawn to waste through the uptake cone. A collecting launder in

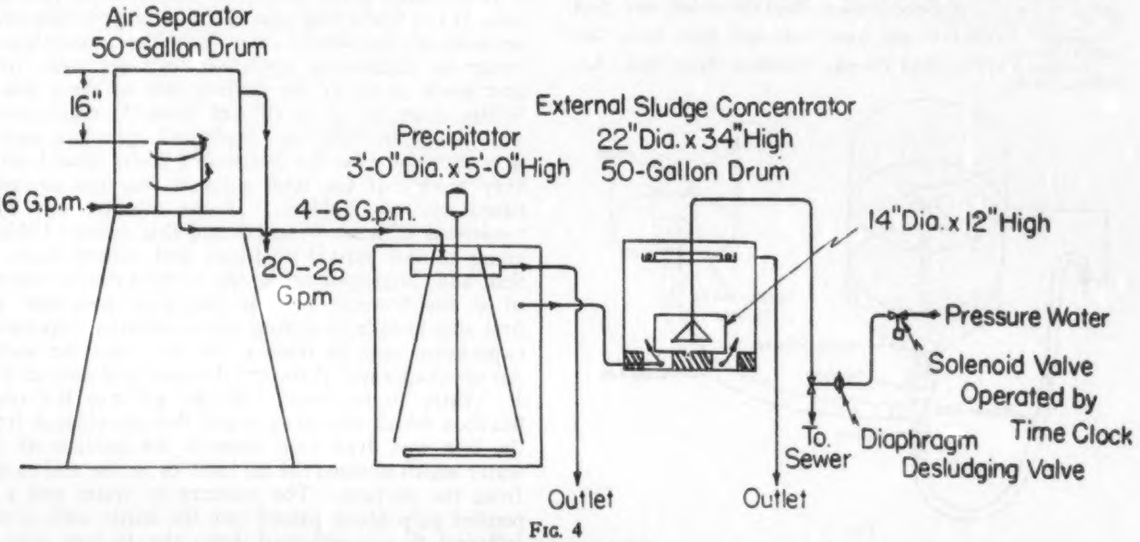

FIG. 4
Diagram of Pilot Plant

the external concentrator allowed the passage of clear water out of the concentrator. Consequently, in those tests where the concentrator was used this effluent was a part of the output of the unit as a whole.

TABLE I.—LABORATORY TEST DATA

	Influent to 5-Gallon Bottle				Effluent from 5-Gallon Bottle			
Number	Source	pH	Temp. °F.	Solids Composite p.p.m.	Rate ml./min.	Hours Run	Suspended Solids p.p.m.	Solids Removed %
1	Filtrate Pit W.W.	5.4 to 5.7	113	285	1100	3.0	82	72
	Filtrate Pit W.W.	5.4 to 5.7	113	285	800	3.5	78	74
2	Filtrate Pit W.W.	5.5	113	285	1050	1.5	53	81
	Filtrate Pit W.W.	5.5	113	285	1100	2.0	70	76
3	Filtrate Pit W.W.	5.6	108	273	1025	1.5	76	72
	Filtrate Pit W.W.	5.6	108	273	1050	2.5	52	81
	Filtrate Pit W.W.	5.6	108	273	900	3.5	38	86
4	½ F.P.W.W. ½ Fresh W.	6.5	104	210	1200	1.0	90	57
	½ F.P.W.W. ½ Fresh W.	6.5	104	210	1100	2.5	54	74
5	½ F.P.W.W. ½ Fresh W.	6.8	104	191	1050		47 at pH 6.8	75

Notes: Run No. 3—Sludge body after end of test=2880 p.p.m. or concentration of 10.5 to 1. Spot test on main sewer leaving mill run No. 3=1.54 pounds per thousand gallons=185 p.p.m. Composite of 6 hours on main sewer run Nos. 5 and 6=236 p.p.m. at 7.0 pH.

In the first fifteen runs the feed consisted of groundwood mill white water taken from one of the supply pumps. In runs 16, 17, and 18, the feed to the headbox was supplied from a portable gasoline pump which picked up part of the total waste effluent passing from the mill. As far as possible, test runs were made on a 24-hour basis. However, the usual amount of minor difficulties cut some of these runs down to shorter periods. The purpose of the pilot plant operation was to determine the effect of the variables encountered in the sewer, such as concentration of suspended solids, temperature, pH, etc., and to establish the clarification mannerisms of this type of equipment in terms of gallons per minute per square foot of area, the effect of velocity, and to get some idea of the maximum sludge concentration which could be handled. With this in mind, the pilot plant operation was split into two phases. The first phase consisted of operation of the precipitator alone without external sludge concentration and the second phase with external sludge concentration.

TABLE II.—SUMMARY OF LOG SHEETS OF PRECIPITATOR PILOT PLANT ON WASTE WATER CLARIFICATION

				Solids in Pounds per Thousand Gallons		
No.	Hours Run	Temp. °C.	pH	Influent to Precipitator	Effluent of Precipitator	Blowoff of Precipitator
1	4	47	5.3 to 5.4	2.4 to 7.9	0.6 to 0.8	5.0 to 8.0
2	21	47	4.9 to 5.3	2.2 to 7.1	0.2 to 2.2	2.7 to 8.7
3	23	47 to 48	4.8 to 5.1	2.6 to 4.5	0.4 to 1.8	5.2 to 7.4
4	23	40 to 48	4.9 to 6.0	2.8 to 6.9	0.2 to 1.0	6.5 to 10.8
5	6	43	....	3.5	0.1 to 0.5	7.8 to 10.6
6	13	47	....	2.4 to 3.5	0.4 to 0.9	5.8 to 7.8
7	22	41 to 46	....	2.5 to 3.1	0.5 to 1.9	7.2 to 10.3

RATE IN GALLONS PER MINUTE

No.	Rate Influent	Desludging from Precipitator	Agitator R.p.m.	Solids Removed %	Remarks
1	3.5 to 4.5	....	22.5	70 to 80	White water
2	2.4 to 4.5	0.7 to 0.9	22.5	54 to 91	White water
3	3.3 to 4.3	0.7 to 1.3	22.5	50 to 85	White water
4	3.2 to 3.8	1.1 to 1.2	22.5	68 to 91	White water
5	3.5	1.2	22.5	86 to 97	White water
6	4.0 to 4.4	1.2	22.5	73 to 85	White water
7	4.0	1.0	22.5	65 to 83	White water

Table II is a summary of typical data of the precipitator operation. As can be seen from these data, there was considerable fluctuation of the solids content of the mill effluent from hour to hour (the sampling cycle through all of the runs). The effluent from the precipitator likewise varied from hour to hour which in turn affected the value of the per cent solids removed. A graph of the solids content to and from the precipitator for each hour during these various runs showed that a sudden increase of solids content in the mill sewer for a short period of time did not materially increase the solids content of the effluent from the precipitator although increases of solids content in the mill sewer for a rather prolonged period of time did increase the solids content of the effluent from the precipitator. This accounts for the rather wide variation in the range of the per cent solids removed as shown in Table II. Although run No. 2 varied from 54 to 91%, removal of solids, run 4 varied only from 68 to 91% removal of solids. Analysis of the hourly values showed that this improvement in operation was caused by maintaining a constant rate of flow rather than by the effect of the concentration of solids in the water coming to the precipitator. It was soon seen that the operation of the precipitator alone did not allow a sufficient concentration of the sludge. The ratio of sludge concentration to solids in the influent was only about three or four to one which meant that some 25% of the water passed to the precipitator would have to be blown out to remove the accumulated fiber. Accordingly, the outside concentrator was installed and started in operation on run No. 8.

Table III is a summary of the typical data of the precipitator operation with an outside concentrator. As can be seen from the data, the concentration of the sludge blow-off increased to between twenty and thirty times the concentration of the influent to the precipitator. This meant that the volume of water which had to be blown off from the precipitator and concentrator as a unit was reduced to a figure well within reason. The operation of the precipitator in this second phase of the pilot plant work continued to be typical of the operation in the first phase. The per cent solids removed the precipitator varied over a fairly wide range of values depending on the variables of the operation.

Because of the multitude of data collected, a summary of the observations of the effect of the varia-

TABLE III.—SUMMARY OF LOG SHEETS OF PRECIPITATOR PILOT PLANT ON WASTE WATER CLARIFICATION

				Solids in Pounds per Thousand Gallons		
No.	Hours Run	Temp. °C.	pH	Influent to Precipitator	Effluent of Precipitator	Sludge Blowoff from Concentrator
8	23	41 to 56	....	2.0 to 3.0	0.1 to 1.9	....
9	21	48 to 49	....	2.6 to 3.0	0.5 to 3.2	....
10	13	37 to 45	....	2.3 to 3.3	0.3 to 2.6	32 to 33
11	8	37 to 42	6.6 to 7.1	1.7 to 2.5	0.2 to 1.0	21 to 53
12	22	40 to 49	5.6 to 6.6	2.3 to 3.2	0.2 to 1.4	40 to 50
13	24	40 to 43	5.5 to 6.7	2.3 to 8.4	0.4 to 2.9	21 to 34
14	17	43 to 48	5.5 to 7.3	2.2 to 3.2	0.3 to 2.0	....
15	18	46 to 48	6.0 to 6.2	2.3 to 3.6	0.2 to 0.7	25 to 42
16	13	37 to 40	7.6 to 7.7	2.1 to 4.8	0.3 to 0.7	20 to 68
17	24	40 to 41	7.4 to 7.6	1.9 to 2.6	0.2 to 0.7	30 to 67
18	24	35 to 41	7.0 to 7.5	1.6 to 3.5	0.2 to 0.5	30 to 66

RATE IN GALLONS PER MINUTE

No.	Rate Influent	Desludging from Concentrator	Agitator R.p.m.	Solids Removed %	Remarks
8	3.1 to 3.7	0.3 to 0.7	22.5	50 to 94	Concentrator installed
9	3.8 to 4.0	0.15	14	50 to 83	....
10	3.7 to 4.0	.....	14	34 to 92	Same
11	3.8 to 5.0	.....	14	76 to 89	White water 25% dilution
12	4.2 to 6.5	.....	14	50 to 94	Same
13	6.1 to 6.9	.....	14	50 to 85	Same
14	5.0 to 7.2	.....	14	40 to 86	Same
15	4.4 to 5.3	.....	14	......	Same
16	5.1 to 6.8	.....	14	60 to 85	Sewer water
17	5.8 to 7.7	0.2	14	70 to 94	Sewer
18	5.5 to 7.2	0.3	14	77 to 99	Sewer

bles will be made rather than giving a set of tables. It was found in general that the variations of pH as such in the mill effluent did not materially affect the clarification operation. As explained before, it was found that changes in concentration of the suspended solids affected or did not affect the operation depending on the duration of time for which the solids content stayed at its new value. A sudden increase of solids content in the mill effluent for just a few minutes was absorbed by the buffering action of the volume of water in the precipitator while increases of a longer duration would make the precipitator effluent somewhat murky. Changes in temperature of the mill effluent was the variable that affected the operation most. A sudden increase in temperature of such a duration that gave an appreciable temperature difference between the influent to the precipitator and the effluent from the precipitator caused the sludge blanket to break loose and thus contaminate the effluent. This was apparently caused by the decrease in density of the sludge blanket in the bottom of the tank when the temperature rose which allowed this stratum of a lower density to rise into the cooler upper portions. It was also found that a sudden increase in velocity caused by an increase in the rate of flow into the unit would cause the sludge blanket to lift and expand and contaminate the effluent.

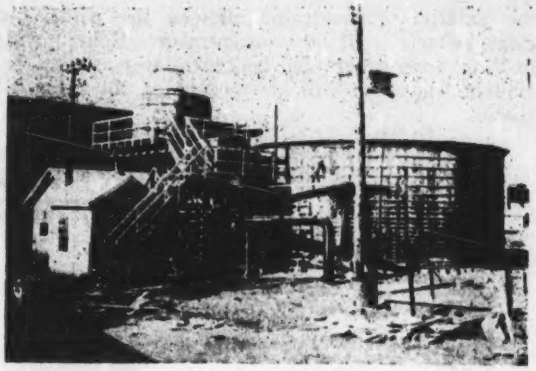

Fig. 6
Buildings Housing Unit

Industrial Size Clarifier

Based on the experience gained in the laboratory experiments and the operation of pilot plant in the field, it was decided to construct a full size industrial unit. The plant was designed to deliver 1180 g.p.m. and remove at least 85% of the suspended solids contained in the influent. The port rate was to be 4.95 gallons per square foot of collecting area, and the surface rate was to be 1.03 gallons per square foot of exposed water surface. The retention time was to be 120 minutes, and the sludge concentrator volume to be 1,590 cubic feet. The same problems were to be overcome in the operation of the large unit that had been encountered with the smaller units. First, some means had to be provided for collecting the water from the 36-inch main sewer line and elevating it to the operation point. Second, the air had to be removed from the feed before it entered the clarifier. Third, means had to be provided to run the unit as a whole at a more or less constant rate of flow in order to avoid sudden changes of velocity within the clarifier. Figure 5 shows the flow diagram of the unit, and the manner in which the three primary problems were solved. A concrete well was built around the 36-inch sewer with a dividing wall present to house the 3,000 g.p.m. pump and motor. After the well was completed, a 10-foot section of the 36-inch sewer was simply removed and replaced with a perforated screen which was revolved by a chain and spur gear drive. The water is picked up from the suction well and pumped to the air removal tank where a constant overflow is maintained back to the suction well. The feed to the clarifier is taken off below the surface and regulation of the flow is carried out by a valve between the headbox and the clarifier. Distribution of the influent is through the circular ring underneath the main bottom baffles at six equidistant points around the circumference of the distributor. The clarified water flows into the collectors and from there into the weir box. Adjustment of this weir to allow a slight overflow of clear water back to the suction well gives any decided quantity of clarified water to the kraft pulp mill where it is used just as if it were fresh water. The sludge withdrawal piping shown in the cross section takes out of the concentrator section at eight equidistant points around the circumference of the concentrator. Figure 6 is an external view of the clarifier. The small house right by the steps which is not shown on the

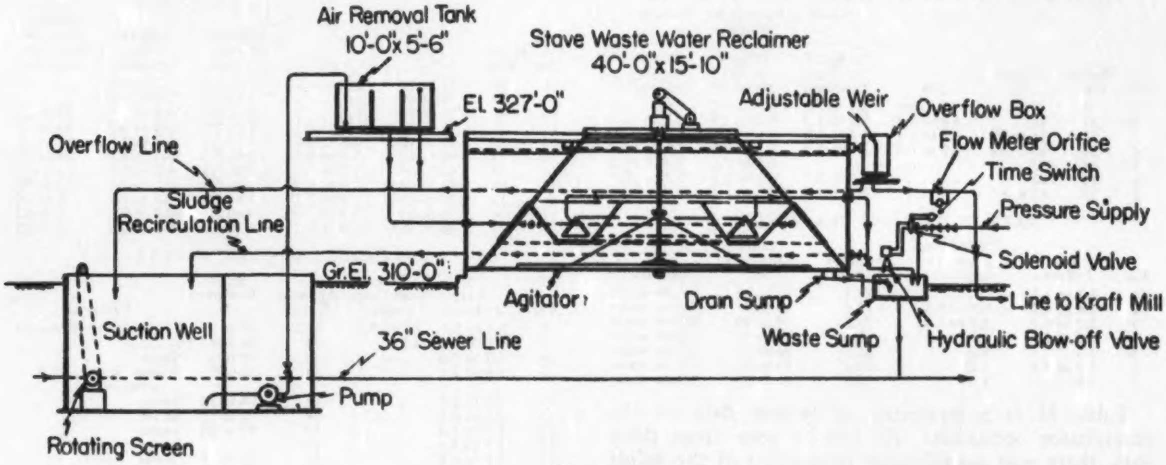

Fig. 5
Flow Diagram of Commercial Unit

flow diagram houses the flow meter and a chlorinator which is used for sterilization of the entire system. The blow down valve mechanism consists of a time clock, solenoid valve, and hydraulic valve to desludge the concentrator section for 2 minutes on a 20-minute cycle. A 2-inch line is tied in just above the gate valve on the blow down piping to allow a small amount of recirculation of the sludge back to the suction well. Figure 7 illustrates the results of typical operation of the clarifier. The tubes from left to right are grab samples taken during normal operation of the influent to the clarifier, the effluent from the clarifier, and the sludge blow down. At the time these samples were taken, the unit was running at 1200 gallons per minute and no flocculating agents or chemicals of any kind had been fed to the system. No extraneous chemicals or materials are used to aid clarification of the suspended pulp present in the influent. The results from hundreds of tests made hourly on the operation of the clarifier show that the average influent will contain some 2 or 3 pounds per thousand gallons of filterable solids and that the effluent will contain 0.1 pounds per thousand gallons or less. The sludge blowoff will average about 50 pounds per thousand gallons.

The filterable solids present in the main sewer consist mainly of groundwood fines originating as white water leaving the groundwood mill and news machine. There are also unbleached kraft fibers present which come from the cylinder machine turning out pulp. The usual ratio of groundwood to chemical pulp is about two to one.

Operating Experiences

When the unit was first started up in December of 1943, it was found that the effluent contained as high as 1 pound per thousand gallons of suspended solids which proved to be groundwood rejects from the secondary screens in the groundwood mill. It was soon found that these coarse rejects did not have the property of self-flocculation on large scale operation, and they were accordingly diverted to a sewer that bypassed the clarifier entirely. The amount of water bypassed was small and of no consequences to the operation as a whole. During the initial periods of starting up the clarifier, various speeds of agitation were employed, and it was found that the speed of agitation had no bearing on the operation of the clarifier. Intermittent desludging versus continuous desludging was studied but it was found that the intermittent desludging was preferable as the relatively large volume of water blown out in a relatively short period of time gave high velocities within the concentrator section which acted to scour the bottom and thus keep the concentrator free and the pulp in a fluid condition.

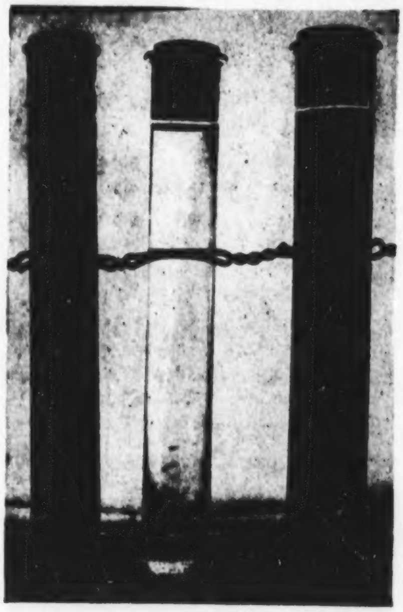

Fig. 7

Samples Taken during Operation—A. Influent to Clarifier. B. Effluent from Clarifier, and C. Sludge Blow-Down.

After about 2 months operation, it was noticed that profuse slime growths were coating the collecting troughs and stopping up the holes with a consequent reduction in flow. A chlorinator was installed and chlorine injected at two points. Approximately 150 pounds of chlorine per day was injected into the riser leading to the air removal tank and approximately 50 pounds per day was injected into the clarified water at the adjustable weir box in order to protect the kraft pulp mill from slime infection. The chlorine application was found to be completely satisfactory and, in this particular case, was superior to any other type of slime prevention.

After the technical service department had operated the clarifier for some 6 months, and the initial difficulties disposed with, the operation was turned over to the pulp and paper mill operating crews. The unit was included as part of the mill water system, and as it had been found that an operator was not required in continuous supervision; the auxiliary fireman from the power house makes a tour of inspection every 4 hours to see that the motors and pumps are running, checks the bearings, and sees that the desludging system is working. As the feed to the clarifier comes from the groundwood and newsprint mills, and as the effluent from the clarifier is utilized by the kraft pulp mill, the two mills work in cooperation to operate the clarifier in the event that something goes wrong and the unit must be shutdown, started up, etc. On a few occasions, the effluent from the clarifier has become contaminated with pulp from the sludge blanket and this was immediately noticed by the operators in the kraft mill washroom. On these occasions, the pulp mill tour boss merely switched from clarified water to the fresh water system and allowed the clarifier to settle down before it was cut back into the kraft mill.

Normal shutdowns of either of the paper machines do not affect the quality of the clarified water. Although a large stock load is suddenly thrown on the system by the dumping of headbox, wire pit, or vats, it is of short enough duration to be absorbed by the sludge bed. Try cocks inserted in the side of the tank show that the sludge bed in normal operation extends about two-thirds of the way up the tank, although it may rise and fall a few feet either way from time to time.

The following operating costs have been arrived at over a period of six months operation. Two hundred pounds of chlorine per day at $3.50 and $1.00 a day for repair labor and material, bring the expendable materials to a total of $4.50 a day. Power requirements are estimated at $2.36 per day which brings the overall total to $6.86 per day. Based on 1000 gallons per minute, the resulting cost is ¢0.51 per thousand gallons.